VOL. XXIX 1916

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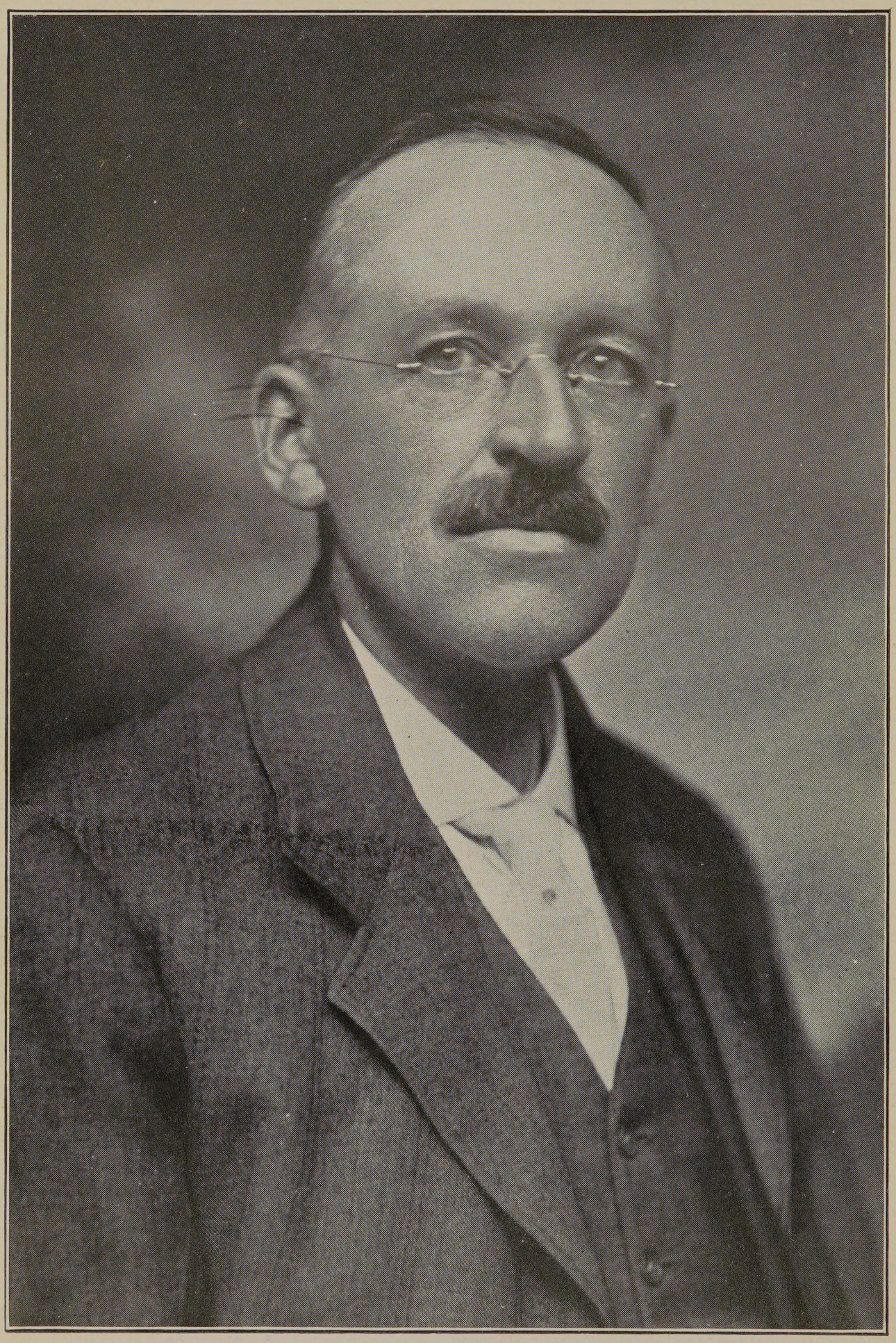

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

VOLUME XXIX

157571

TWENTY-NINTH GENERAL MEETING

WASHINGTON, D. C., APRIL 27, 28, 29, 1916

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AT THE OFFICE OF ITS SECRETARY

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VOLUME XXIX. 1916.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE TWENTY-NINTH GENERAL MEETING OF THE SOCIETY, HELD IN WASHINGTON, D. C., APRIL 27, 28 AND 29, 1916.

Number of members registered, 117; number of guests registered, 138; total, 255.

PROCEEDINGS OF WEDNESDAY, APRIL 26.

Although the meeting of our Society did not commence until the 27th, the American Institute of Electrical Engineers held a meeting at the New Willard Hotel on the afternoon and evening of April 26th, at which the members of this Society were cordially invited to be present. The sessions at 2.00 P. M. and 8.15 P. M., in the New Willard Hotel, were devoted to a discussion of the water-power question and its relation to various industries. The papers presented were as follows:

Address by President John J. Carty.

Electrochemical Industries and Their Interest in the Development of Water Power: Lawrence Addicks.

Water Power Development and the Food Problem: A. S. Cushman.

Relation of Water Power to Increased Transportation: L. B. Stillwell.

The Relation of Water Power to the National Defense: W. R. Whitney.

The Water Power Situation, including Its Financial Aspect: Gano Dunn.

Registration of members and guests of the American Electrochemical Society began in the New Willard Hotel at 6.00 P. M.

A meeting of the Board of Directors, at dinner, was held in the New Willard Hotel at 6.30 P. M.

A meeting of the Publication Committee was called for 10.00 P. M.

PROCEEDINGS OF THURSDAY, APRIL 27.

The meeting was called to order by President L. Addicks in the red room of the New Willard Hotel at 9.45 A. M. The President made the following remarks:

"In opening this, our Twenty-ninth General Meeting, I am glad to say that I think the Society is in a very satisfactory condition. Financially, it has passed through a difficult period of readjustment, to get its income equal to its increased expenses. On the membership side, I think we are doing very well. While the hard times of a year or two ago caused a good many of our members to drop away, we have replenished all we lost, and there are an unusual number of new members joining each month. On the technical side of our work, I do not think we have ever had such a liberal and high grade offering of papers as we have for presentation at this meeting."

It being the annual business meeting of the Society, the reading of the minutes of the last business meeting was called for, but was dispensed with, they being approved as printed in the last volume of Transactions.

The report of the Board of Directors, including those of the Secretary and Treasurer, was read by Secretary Richards, and accepted for publication in the Proceedings of the meeting, to which it is appended.

Dr. Baekeland, of the Patent Committee, presented the following report, which was read by the Secretary:

"Since the last meeting of the American Electrochemical Society nothing of real importance has occurred on the subject of patent legislation.

"It is very probable that the question of patent reform will be taken up as soon as more urgent matters are disposed of. It seems hardly possible, however, to take up thoroughly the subject of patent reform during the present legislative session.

"In the meantime, the so-called Paige Bill has again been presented for consideration before the House of Representatives. Although this bill is conceived with the best of intentions its de-

fects are such as to do incomparably more harm than good. The bill has been thoroughly discussed last year before the House Committee on Patents, and for a time it seemed as if this bill were to be withdrawn. Aside from the arguments which were presented against this bill by the representatives of your Committee there has been published by Dr. Bernhard C. Hesse an exhaustive article on this subject in which all further data can be found. This article appeared in the Journal of Industrial and Engineering Chemistry, Vol. 7, No. 11, p. 963, November, 1915.

"The unfortunate part of all such bills is that they merely constitute patchwork devised without any comprehensive idea of the general situation and which, therefore, unknown to their authors, embody dangers which would tend to cripple our whole patent system and make it still worse than it is.

"We fear that this situation will persist as long as the matter of systematic patent reform is not entrusted to a non-partisan, non-political, technical commission of qualified men, including representatives of the public, the manufacturers, the inventors, the Federal Courts, and the patent bar.

"This suggestion along the lines of efficiency, which seems simple enough to chemists and engineers, does not, however, appear to meet the views of our legislative bodies, which are overwhelmingly composed of lawyers. This once more brings out how a most democratically planned republic may lead to inefficiency if, for some reason or another, the people prefer to elect, almost exclusively, lawyers to act as their representatives in Congress and in the Senate. The matter resolves itself simply to what is more desirable—government by lawyer-politicians, or government by experts?

"A general plan of revision of our patent laws could hardly be carried out without taking into consideration treaties with foreign countries. The very fact that practically all important foreign industrial countries are now at war makes it impossible to undertake anything of the kind at present.

"Your Committee holds itself ready to take the first opportunity, whenever conditions warrant it, to co-operate with similar committees of other societies for the advancement of any constructive patent legislation which will tend to bring our patent system up to the requirements of modern conditions.

"It gives great satisfaction to the Committee to mention that the present Patent Commissioner has done much to simplify and increase the efficiency and operation of the Patent Office; it should be stated also that the present Chairman of the House Committee on Patents has given considerable study to the patent situation, and is unusually well prepared to investigate the merits of any subjects brought before his Committee."

Under the head of new business Dr. C. G. Fink extended to the Society, on behalf of the members of the New York Section, a cordial invitation to meet in September, 1916, in New York City, in conjunction with the National Exposition of Chemical Industries. The invitation was received with thanks and referred to the Board of Directors for consideration.

President Addicks then announced that at the meeting of the Board of Directors, held the previous night, a committee on Public Relations was appointed, to consist of the President of the Society as Chairman, and all of the past-presidents as members. The purpose of the Committee is to co-operate in legislative matters. They expect to inform the various committees of Congress that they stand ready to appear singly or in numbers, to be heard on any question on which the Committees of Congress desire information along broad electrochemical lines.

[The appointment of this Committee was endorsed by the Society on Saturday, April 29th. See Proceedings of that day, page 10.]

G. A. Roush was then called upon for the report of the annual election of officers, which was submitted as follows:

To the Members of the American Electrochemical Society:

GENTLEMEN: Following is a list of the votes cast in the election of officers for the year 1916-1917:

President: F. A. J. FitzGerald, 182; C. Hering, 1; C. G. Schluederberg, 1; E. F. Smith, 1; E. R. Taylor, 1; F. J. Tone, 1.

Vice-President: C. G. Schluederberg, 149; A. L. Walker, 149; F. J. Tone, 144; W. L. Miller, 58; J. W. Browne, 39; F. A. J. FitzGerald, 10; I. Langmuir, 1; E. F. Roeber, 1.

Managers: W. D. Bancroft, 154; E. F. Roeber, 125; Carl Hering, 110; Wm. Brady, 90; H. B. Coho, 46; F. C. Frary, 29; F. J. Tone, 10; A. B. Marvin, 1.

Treasurer: P. G. Salom, 184; C. A. Winder, 1.

Secretary: J. W. Richards, 185; A. T. Hinckley, 1; G. A. Roush, 1; C. G. Schluederberg, 1.

Respectfully submitted,

S. S. Seyfert,
G. A. Roush,
A. S. Callen.

The Chairman then announced the following elections, as the result of the report of the Tellers:

President: F. A. J. FitzGerald.

Vice-Presidents: C. G. Schluederberg, A. L. Walker, F. J. Tone.

Managers: W. D. Bancroft, E. F. Roeber, C. Hering.

Treasurer: P. G. Salom.

Secretary: J. W. Richards.

President-elect FitzGerald was then called upon by President Addicks to act as Chairman *pro tem.,* while President Addicks delivered the Presidential address, as printed in full in these Transactions.

Reading of papers and discussion thereon were then taken up, papers being presented by the following, and discussed as printed in these Transactions:

A symposium on Co-operation in Industrial Research by L. Addicks (read by the Secretary), F. A. Lidbury, W. D. Bancroft, W. H. Walker, D. A. Lyon (read by the Secretary), L. H. Baekeland (read by the Secretary), and W. R. Whitney (read by the Secretary); papers by W. D. Bancroft, E. D. Ardery (abstracted by the Secretary), G. Ornstein (abstracted by Dr. C. G. Fink), and W. M. Grosvenor (abstracted by Prof. G. A. Roush).

At the close of this session luncheon was taken in the blue room of the New Willard Hotel.

At 2.00 P. M. the afternoon session was called to order in the red room of the New Willard Hotel, Prof. W. D. Bancroft in the chair.

Reading of papers and discussions were taken up, papers being presented by the following and discussed as printed in these Transactions: A Symposium: Niagara Falls Power and Ameri-

can Industries, by I. R. Edmands, F. J. Tone, A. H. Hooker and W. S. Landis; an illustrated address on Reclamation Service Water Power, by Dr. A. P. Davis, Chief of the Reclamation Service; papers by W. E. Ruder, C. H. Vom Baur, W. M. MacKnight (read by title), F. M. Sebast and G. L. Gray (read by title), and O. L. Kowalke (read by title).

The evening session was called to order at 8.00 P. M., Mr. J. H. Finney, of Washington, in the chair. Mr. J. H. Pierce, of Seattle, Washington, delivered before a large audience an illustrated lecture on Water Power Development and the Electrochemical Industries.

PROCEEDINGS OF FRIDAY, APRIL 28.

The meeting was called to order at 9.45 A. M. in the red room of the New Willard Hotel, President Addicks in the chair. Papers were presented by the following and discussed as printed in these Transactions: C. W. Bennett and W. S. Burnham, C. W. Bennett, W. D. Bancroft (two papers), W. C. Arsem, N. K. Chaney and Irving Langmuir.

The afternoon was spent on a steamboat trip to Mount Vernon, which was greatly enjoyed by all participating.

The evening session was called to order at 8.30 P. M., in the Mezzanine Room of the New Willard Hotel, Dr. A. S. Cushman in the chair. Papers were presented by the following and discussed as printed in these Transactions: D. A. MacInnes (read by title), C. W. Bennett and E. L. Mack, W. G. Cady, W. A. Darrah (abstracted by C. G. Schluederberg), W. McF. Moore (read by title), W. H. Walker, J. Aston (read by title), and B. McCollum and G. H. Ahlborn (read by title).

PROCEEDINGS OF SATURDAY, APRIL 29.

The meeting was called to order at 10.00 A. M. in the Assembly Hall of the Electrical Building at the Bureau of Standards, President L. Addicks in the chair. Dr. H. F. Stratton, Director of the Bureau of Standards, made the following speech of welcome:

"*Mr. Chairman and Gentlemen:* It gives me very great pleasure to meet with you this morning, and to have you meet at the Bureau. The Bureau of Standards is brought very closely in

contact with many associations of this kind, and I am more and more impressed with the value of them.

"We have with us this morning the American Electrochemical Society. There has always been too great a breach between physics and chemistry, especially in our educational institutions; there has been a wide gap between these two sciences. Fortunately, in the application of them they cannot be separated so widely, and you people are destined to bring them together more than any other agency. We at the Bureau are also interested. We have tried to do all we can to amalgamate physics and chemistry in such a way that the great problems before us can be attacked most efficiently.

"And there is still another phase of your work in which we are greatly interested, and to which, perhaps, we contribute not a little. It is the application of scientific work to the industries. There is no question in my mind but that our industrial progress in the future will depend almost directly upon the extent to which we apply scientific work and scientific methods. In this we are greatly concerned, and a large portion of the work of the Bureau is devoted to the working out of those scientific problems which will be of benefit to the various industries. Your meeting here this morning is of the greatest assistance to us in this particular phase of our work.

"I wish to extend to you, on behalf of myself and my associates, the most hearty welcome. The laboratories will be open to you, the young men in charge of your parties have arranged several exhibits, and every courtesy in our power will be shown to you. We are very glad to have you with us, we hope you will come again, and that, as individuals, you will help us in the various lines of work in which we are jointly interested. I thank you very much."

Dr. Carl Hering presented the following resolution, which was duly seconded and passed:

RESOLVED, That the American Electrochemical Society endorses the essential features and aims of H. R. Bill No. 528, having for its object the adoption of the centigrade scale of temperature as the standard scale in all United States Government publications, and the ultimate discontinuance of the Fahrenheit scale after a reasonable transition period.

Dr. Carl Hering: There are several features to this resolution and the bill referred to that I think ought to be explained, so that it will be better understood. We have with us today Dr. Waidner, of this Bureau, who is much more familiar with the history of this bill, and I am sure that he can tell you in a few words a great deal more about it than I could.

Dr. Waidner then explained the nature of the bill at length.

Papers were then read by the following and discussed as printed in these Transactions: W. R. Ingalls, O. W. Storey (presented by F. A. Lidbury), G. H. Hogaboom, F. C. Mathers, E. H. Stuart and E. G. Sturdevant (abstract presented by Mr. Hogaboom), O. P. Watts (presented by C. G. Fink), F. C. Mathers and B. W. Cockrum (read by Mr. C. G. Schluederberg), F. C. Mathers and B. W. Cockrum (read by Mr. C. G. Schluederberg), F. C. Mathers and J. R. Kuebler (presented by Prof. Roush).

After the papers were read and discussed, W F. Hillebrand gave the Society a very interesting talk on Gallium, accompanied by an exhibition of specimens.

W. F. Hillebrand: There is something I have here which I thought might be of some interest, although it has not been obtained by electro-deposition. Nevertheless, if the metal gallium does become commercially available, it may be important to determine the conditions under which it can be best utilized as an electrolytic deposit.

The metal is obtained, as perhaps most of you know if you have read the article by Mr. Scherrer and myself in the April number of the Journal of Industrial Engineering Chemistry, by the distillation of the spelter obtained from certain ores at Bartlesville, Oklahoma. The gallium comes over with the zinc in the first rapid distillation at 1350° C., and remains to a large extent behind when the spelter is redistilled at 1000°. The gallium alloy then sweats out at the surface of the "dross," and in the course of a few weeks is observed there in the form of semi-liquid drops. It seems to carry a little indium according to Browning and Uhler, which may be 10 percent. My own test would indicate a very much smaller quantity, but that would prove nothing, because we may have had material derived from somewhat different ores or mixtures of ores. The superintendent of the Bartlesville Zinc Company believes that we are not likely

to have a permanent source of gallium, as he does not think that conditions will continue under which it will be necessary to refine the first distillation of spelter. One of the characteristic and striking properties of the metal is that it wets glass and porcelain. This tube is only partly full (there are about 25 grams of gallium in it), yet it looks entirely silvered. Whether the property of wetting such surfaces will hold for perfectly pure gallium is something that remains to be determined, and it may be of very considerable interest, because if perfectly pure gallium does not wet glass or quartz, it is conceivable that it may be used as a thermometer liquid for high temperatures, above temperatures at which glass fuses, provided we use quartz bulbs and capillaries.

You see here the normal condition of the gallium in its undercooled condition; it melts at about 30 degrees, but can be undercooled and maintained in that condition indefinitely, even at temperatures as low as zero.

The metal in this bottle originally coated or silvered it, as you see in the case of the tube, but the addition of a little dilute hydrochloric acid or sulphuric acid immediately causes it to leave the surface of the glass and collect in a liquid mass; there is a slight evolution of hydrogen, but very slight indeed; it then looks like mercury, but, of course, the difference in specific gravity is very great.

Carl Hering: Where does the gallium go when zinc is refined electrolytically?

W. F. Hillebrand: No efforts have been made to determine that so far as I know.

Joseph W. Richards: Although this is so expensive, yet the fact that it is liquid at ordinary temperatures may make it useful to the electrochemist for investigating some reactions for which mercury is not suitable. The suggestion has been made that easily melted alloys might be used as cathodes in aqueous solutions at temperatures toward 100° C., but here we have a metal having entirely different properties from mercury, which can be used experimentally at ordinary temperatures.

W. F. Hillebrand: It is interesting to see a metal liquid at the ordinary temperature which has practically no vapor pressure at 1000° C., and does not boil at 1600°.

Joseph W. Richards: I would ask one other question, since the fact that it can be supercooled permanently below 30 degrees is so unusual, I would like to know a little more about it. Under what conditions does it freeze at 30 degrees?

W. F. Hillebrand: When deposited electrolytically from an alkaline solution it is a solid. The under-cooled liquid can be solidified by inoculation with a particle of solid gallium.

Mr. A. H. Hooker then presented the following resolution, which was duly seconded and passed.

Resolved, That this Society endorses the action of its Board of Directors in appointing the Past-Presidents of the Society, under the Chairmanship of the President, as a Committee on Public Relations, and expresses its confidence in that Committee and its ability to represent the Society in giving advice to legislative committees and other bodies.

F. J. Tone: I desire to second the resolution, and in doing so I desire to take the opportunity of saying that technical societies have a great opportunity today to make their opinions and their influence felt on public questions. I hope that this Society will avail itself of this opportunity to the greatest possible extent.

Mr. F. A. Lidbury offered the following resolution, which was put to vote and unanimously adopted:

Resolved, That the American Electrochemical Society expresses its hearty appreciation of the services of its Local Committee in arranging the details of this Twenty-ninth General Meeting of the Society, also extends its thanks to the Ladies' Committee for their entertainment of the visiting ladies, to Mr. J. H. Pierce and Director A. P. Davis for their instructive lectures, to the manager of the New Willard Hotel for the use of its assembly room, and finally, for the invitation extended to it by the Bureau of Standards, whose hospitality we are at present enjoying.

The co-operation of all the above has resulted in one of the most interesting and successful meetings ever held by the Society.

There being no further business, President Addicks declared the twenty-ninth general meeting closed.

ANNUAL REPORT OF THE BOARD OF DIRECTORS.

To the Members of the American Electrochemical Society:

We submit herewith the annual reports of the Secretary and Treasurer for the year 1915, the former containing the detailed financial statement of receipts and expenditures.

The net decrease in number of members during the year was 20, in spite of the fact of the unprecedented number of 86 having been dropped at the end of the year for non-payment of dues. The financial disturbance incident to the war necessarily limited the growth of the Society, but the increases in the last months of 1915 and the early months of 1916 show that the Society is again gaining ground.

Financially, the Society passed through a difficult period of readjustment to get its decreased income equal to its increased expenses, but this has been satisfactorily accomplished by realizing upon some of the fixed investment of the Society, and finances are at present in a satisfactory condition.

The following are the more important actions taken by the Board of Directors during the past year:

The Society was represented at the Second Panama-American Scientific Congress held in Washington, D. C., December 27, 1915, to January 28, 1916. The delegates were Dr. Carl Hering, with G. A. Roush as alternate.

The membership of members residing in countries now at war shall not be terminated for non-payment of dues until after the conclusion of the war.

The Niagara Falls Section was organized and approved July 23, 1915, its territory being that within a radius of 50 miles from Niagara Falls.

In September President Addicks canvassed the Board of Directors by mail, to comply with the request by the Secretary of the Navy that the Society appoint representatives upon the Naval Consulting Board. President Addicks reported to the Board meeting, September 15th, that Dr. W. R. Whitney and Dr. J. W. Richards had been selected as representatives, with Dr. L. H. Baekeland, President Lawrence Addicks and Professor W. D. Bancroft as alternates. On designating these to the Secretary of the Navy it appeared that Messrs. Whitney and Baekeland had

already been delegated to represent the American Chemical Society, and that therefore Messrs. Richards and Addicks were the delegates to act as representatives of this Society.

After prolonged discussion on methods of reducing expenses and increasing the income of the Society, it was ordered at the Board meeting, October 15th, that, commencing with 1916 Transactions, the bound volumes be *not* sent to all members paying dues, but only to those members who pay $2.50 per volume extra, this charge to be placed on the annual bill as an optional charge. It was further agreed that the minutes of the meetings of the Society, discussions of papers, and list of members be sent in pamphlet form to all members paying dues, so that they would receive in pamphlet form everything contained in the bound volumes. It was also decided that since bound volumes would not be sent to all members of the Society, but only to those paying extra for them, advertisements be omitted from the bound Transactions.

SECRETARY'S ANNUAL REPORT.

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN: In 1915 the Society held two general meetings, one at Atlantic City and Philadelphia, April 22, 23 and 24, 1915, at which the attendance was 71 members and 60 guests, total 131; the second at San Francisco, Cal., September 16, 17, 18, 1915, at which the attendance was 30 members and 33 guests, total 63. The Transactions of the Spring meeting include 21 papers, and those of the Fall meeting 21 papers.

In 1915 there were issued and distributed to our members two volumes of the Transactions: Volume XXVI, the Transactions of the meeting in Niagara Falls, October 1, 2, 3, 1914; Volume XXVII, of the Atlantic City and Philadelphia meeting, April 22, 23, 24, 1915. These volumes contained 270 and 486 pages respectively.

The Transactions of the San Francisco Meeting, September 16, 17, 18, 1915, were issued February 1, 1916, and contained 430 pages.

The edition of the 1915 volumes was 1,500 copies bound in

cloth for distribution to our members; 50 extra copies in sheets for distribution in pamphlet form to authors of papers; 250 copies bound in paper for distribution to the Faraday Society; 500 copies sewed, ready for binding, to be kept in stock.

Complete sets of the Transactions are still on hand, but the stock is rapidly diminishing, and Volumes I, II and III will hereafter be sold at double price, according to action of the Board of Directors.

The stock of Volumes on hand December 31, 1915, was as follows:

Volume	Bound in Cloth	Bound in Paper or Stitched Ready for Binding	Total
I	147	13	160
II	176	0	176
III	84	0	84
IV	108	233	341
V	62	234	296
VI	78	242	320
VII	78	199	277
VIII	95	321	416
IX	95	315	410
X	101	257	358
XI	95	267	362
XII	94	265	359
XIII	112	235	347
XIV	224	251	475
XV	217	224	441
XVI	217	289	506
XVII	154	521	675
XVIII	167	522	689
XIX	37	531	563
XX	36	535	571
XXI	35	554	589
XXII	43	548	591
XXIII	28	543	571
XXIV	42	558	600
XXV	62	539	601
XXVI	84	547	631
XXVII	201	541	742

Condition of the Society in regard to membership in 1915:

Members January 1, 1915		1,377
Elected and qualified as members in 1915		107
		1,484
Resignations in 1915	34	
Deaths in 1915	7	
Dropped for non-payment of dues	86	
	—	127
Members December 31, 1915		1,357

(30 European members have not paid 1915 dues but are kept on the books until after the war.)

Condition, April 27, 1916.

Members January 1, 1916		1,357
Qualified as members, to April 27th	70	
Deaths	1	
Dropped for non-payment of dues	41	
Net increase	—	28
Members, April 27, 1916		1,385

Financial Statement.

January 1, 1915, to December 31, 1915.

Cash assets beginning January, 1915, account		$492 88

RECEIPTS.

Entrance fees	$535 00	
Current dues	4,340 16	
Back dues	159 54	
Advance dues, 1916	1,080 12	
Volumes 1916, paid in advance	755 00	
Sales of publications	1,028 60	
Advertisements	148 74	
Interest on bonds and bank account	278 63	
Miscellaneous	13 44	
Sales of bonds	3,095 88	
Sale of extra reprints	27 50	
		$11,462 61
Total		$11,955 49

EXPENDITURES.

Office printing	$466 96
Express and postage for volumes	316 12
Office postage	316 70
Adv. copies postage	305 00
Faraday postage	30 00
Office expenses	247 11
Office furniture	54 11
Printing of Volume 26	1,241 01
Printing of Volume 27	1,605 45
Advance copies	757 13
Engraving	250 02
Extra reprints	56 10
Storage and insurance	138 85
Silver for Res. Committee	192 74
Local sections	450 00
Secretarial appropriation	1,500 00
Expenses of meetings	418 04
Publication Committee	25 01
Advertisement commission	2 44
International Tables of Constants	50 00
Payment on note	2,000 00
Cash payment Faraday Society Transactions	328 00
	$10,750 89
Cash balance beginning January, 1916, account	1,204 60
Total	$11,955 49

ASSETS, JANUARY 1, 1915.

Cash balance, January 1, 1915:		
On deposit	$1,154 60	
Cash box	50 00	
Bonds held by the Society	3,102 50	
Unpaid 1915 dues, since paid	205 00	
		$4,512 10
Obligations:		
Printing of Vol. XXVIII	$1,682 31	
Postage and Expressage	169 00	
1916 dues paid in 1915	1,065 01	
1916 volumes paid in 1915	755 00	
		$3,671 32
Present worth, December 31, 1915		$840 78
Fixed assets, furniture and fixtures and stationery (including postage stamps)		100 00
Stock of volumes of Transactions on hand, 12,156 copies		not appraised

TREASURER'S ANNUAL REPORT.

FOR THE YEAR 1915.

Jan. 1, 1915. Cash balance		$492 88	
Jan. 1, 1915 to Jan. 31, 1915:			
Receipts as per statement attached		11,462 61	
			$11,955 49
Expenditures, 1915, as per statement attached			10,750 89
Balance, December 31, 1915			$1,204 60
Dec. 28, 1915:			
Balance Commonwealth Trust Co.		$1,514 93	
Less checks not in, Nos.			
703	$500 00		
704	171 12		
705	100 00		
706	24 61		
707	27 00		
708	113 59		
		$936 32	
		$578 61	
Dec. 31, 1915. Bal. E. P. Wilbur Trust Co.		575 99	
Balance in cash drawer		50 00	
			$1,204 60

We have examined the above statement of account and receipts and expenditures for the year 1915 and find the same to be correct.

We also report $3,000 Philadelphia Electric Gold Trust Certificates in the box of the Society in the Safe Deposit Vaults of the Commonwealth Title Insurance and Trust Company, Philadelphia, Pennsylvania.

CARL HERING,
S. S. SADTLER, } *Auditors.*

MEMBERS AND GUESTS REGISTERED AT THE TWENTY-NINTH GENERAL MEETING.

Members.

P. O. Abbe
Lawrence Addicks
J. C. Andrews
F. L. Antisell
Wm. C. Arsem
Walter Arthur
James Aston
C. G. Atwater
L. H. Baekeland
T. F. Baily
A. T. Baldwin
W. D. Bancroft
E. H. Bedell
C. W. Bennett
E. R. Berry
E. Blough
W. Blum
Wm. H. Bristol
deCourcy Browne
A. R. Calder
F. K. Cameron
W. H. Carrier
N. K. Chaney
R. B. Chillas, Jr.
G. W. Coggeshall
H. B. Coho
E. A. Colby
W. M. Corse
F. G. Cottrell
J. S. Crider

Twenty-ninth General Meeting of the American Electrochemical Society, Washington, D. C., April 27-29, 1916.

Members (Continued).

Ed. L. Crosby
Wm. J. Cummings
A. S. Cushman
N. E. Dabolt
A. W. Davison
P. K. Devers
Bradley Dewey
F. P. Dewey
H. G. Dorsey
L. C. Drefahl
I. R. Edmands
P. H. Falter
C. G. Fink
J. H. Finney
F. A. J. FitzGerald
Chas. B. Foley
F. C. Frary
H. A. Gardner
A. E. Gibbs
C. B. Gibson
A. McK. Gifford
H. W. Gillett
S. L. Goodale
J. H. Goodwin
C. McC. Gordon
Jos. W. Harris
Carl Hering
A. T. Hinckley
Geo. B. Hogaboom
H. D. Holler
A. H. Hooker
Henry Howard
W. F. Hubley
M. A. Hunter
O. Hutchins
T. Igarashi
B. H. Jacobson
C. P. Karr
H. F. Kleinfeldt
Walter Laib
W. S. Landis
Irving Langmuir
J. N. Lawrence
F. A. Lidbury
C. F. Lindsay
A. F. Lucas
Chas. P. Madsen
W. W. Mann
S. C. Mastick
J. A. Mathews
E. C. McKelvy
F. N. Moerk
Wm. R. Mott
J. M. Muir
Adriaan Nagelvoort
D. L. Ordway
C. A. Orr
Y. Oshima
H. C. Parmelee
Chas. L. Parsons
N. K. B. Patch
H. E. Patten
N. Petinot
Wm. B. Price
J. W. H. Randall
Wm. J. Rich
Jos. W. Richards
E. F. Roeber
G. A. Roush
D. B. Rushmore
C. G. Schluederberg
F. F. Schuetz
S. Skowronski
Fin Sparre
F. N. Speller
H. M. St. John
H. S. Taylor
F. J. Tone
F. M. Turner, Jr.
J. W. Turrentine
G. D. van Arsdale
C. H. Vom Baur
Wm. H. Walker
A. M. Williamson
C. A. Winder
Chas. Wirt
J. A. Yunck

Guests.

Mrs. Lawrence Addicks, E. Orange, N. J.
H. B. C. Allison, Schenectady, N. Y.
Mrs. Wm. C. Arsem, Schenectady, N. Y.
Jas. B. Arthur, Baltimore, Md.
Mrs. J. B. Arthur, Baltimore, Md.
James L. Aupperle, Middletown, O.
Mrs. T. F. Baily, Alliance, O.
E. M. Baker, State College, Pa.
Mrs. W. D. Bancroft, Ithaca, N. Y.
John S. Bates, Montreal, Canada.
H. Beckman, Minneapolis, Minn.
Marcus A. Beeman, Washington, D. C.
W. D. Bigelow, Washington, D. C.
H. J. Blanchard, Niagara Falls, N.Y.
M. F. Bowen, Washington, D. C.
Chas. W. Burrows, Washington, D. C.
W. G. Cady, Middletown, Conn.
J. N. Carothers, Washington, D. C.
S. C. Carrier, New York City.
John J. Carty, New York City.
Liveian W. Chaney, Washington, D. C.
J. K. Clement, Pittsburgh, Pa.
J. H. Clough, Schenectady, N. Y.
Mrs. G. W. Coggeshall, Washington, D. C.
Mrs. H. B. Coho, New York City.
Mrs. E. A. Colby, Newark, N. J.
G. E. Condra, Lincoln, Neb.
Mrs. G. E. Condra, Lincoln, Neb.
E. F. Cone, New York City.
W. C. Cope, Pittsburgh, Pa.
Mrs. O. T. Cortwright, Washington, D. C.
Mrs. F. G. Cottrell, Washington, D. C.
James A. Cowle, Washington, D. C.
Jasper E. Crane, Arlington, N. J.
R. A. Crider, Cleveland, O.
T. E. Crossman, New York City.
Mrs. W. J. Cummings, Haskell, N. J.
H. T. Darlington, Philadelphia.
C. Dittmar, New York City.
C. O. Fairchild, Washington, D. C.

Guests (Continued).

B. Felician, Philadelphia.
Mrs. John H. Finney, Washington, D. C.
Mrs. F. A. J. FitzGerald, Niagara Falls, N. Y.
H. C. Flanigan, New York City.
P. K. Fletsher, Detroit, Mich.
T. S. Fuller, Schenectady, N. Y.
C. G. Gilbert, Washington, D. C.
S. Goldstein, New York City.
Mrs. S. L. Goodale, Pittsburgh, Pa.
Mrs. J. H. Goodwin, Fremont, O.
L. H. Greathouse, Washington, D. C.
J. J. Haas, Washington, D. C.
Mrs. J. J. Haas, Washington, D. C.
Jas. O. Handy, Pittsburgh, Pa.
Mrs. Jos. W. Harris, Washington, D. C.
Wm. Hazen, New York City.
N. F. Hillebrand, Washington, D. C.
Carl D. Hocker, New York City.
Rudolf P. Hommel, Bethlehem, Pa.
Mrs. R. P. Hommel, Bethlehem, Pa.
H. B. Howland, Minneapolis, Minn.
Mrs. W. F. Hubley, East Orange, N. J.
F. L. Hutchinson, New York City.
H. Jennings, Washington, D. C.
A. E. Johnson, Washington, D. C.
H. J. Kennedy, New York City.
David A. Keys, Toronto, Canada.
H. B. Knowles, Washington, D. C.
C. P. Landreth, Philadelphia.
Chas. W. Land, New York City.
Mrs. I. Langmuir, Schenectady, N. Y.
I. H. Levin, Newark, N. J.
S. C. Lloyd, Wilmington, Del.
Alfred B. Lort, Washington, D. C.
E. A. Lof, Schenectady, N. Y.
H. G. Mains, Washington, D. C.
Mrs. W. W. Mann, Cleveland, Ohio.
W. J. Marsh, Washington, D. C.
E. McAusland, Washington, D. C.
G. W. Middlekauff, Washington, D. C.
Mrs. F. N. Moerk, Philadelphia.
Roy W. Moore, Schenectady, N. Y.
R. W. E. Moore, Pittsburgh, Pa.
H. J. Morgan, Washington, D. C.
W. E. Mosher, Washington, D. C.
Adolph H. Nietz, Rochester, N. Y.
W. J. O'Brien, Washington, D. C.
Wm. H. Onken, Jr., New York City.
R. L. Patterson, Niagara Falls, N. Y.
Axel Paulsson, Stockholm, Sweden.
Mrs. N. Petinot, New York City.
Ralph W. Pope, Newark, N. J.
Mrs. M. Randall, Baltimore, Md.
F. E. Rasmers, Baltimore, Md.
Henry S. Rawdon, Washington, D. C.
G. T. Reich, Niagara Falls, N. Y.
Malcolm N. Rich, Washington, D. C.
Mrs. W. J. Rich, Washington, D. C.
Dr. E. B. Rosa, Washington, D. C.
C. J. Rottmann, Rochester, N. Y.
Mrs. G. A. Roush, S. Bethlehem, Pa.
O. T. Roush, Jonesboro, Ind.
W. E. Ruder, Schenectady, N. Y.
Mrs. W. E. Ruder, Schenectady, N. Y.
B. Russell, Washington, D. C.
J. A. Scherrer, Washington, D. C.
Mrs. C. G. Schluederberg, Pittsburgh, Pa.
F. Schoenawa, Lichterfelde, Berlin.
T. H. Schoepf, Pittsburgh, Pa.
Edw. Schramm, Washington, D. C.
Jas. Schroeder, Washington, D. C.
Miss Matilda E. Senior, Washington, D. C.
Geo. R. Shepard, Niagara Falls, N. Y.
P. W. Shepard, Washington, D. C.
W. M. Slater, Washington, D. C.
R. B. Sosman, Washington, D. C.
Miss Squire, Washington, D. C.
H. L. Stoll, New York City.
S. W. Stratton, Washington, D. C.
C. S. Taylor, Washington, D. C.
E. E. Thum, Cincinnati, Ohio.
Calvert Townley, New York City.
H. S. Turner, Washington, D. C.
E. S. Van Brunt, Washington, D. C.
Geo. W. Vinal, Washington, D. C.
S. S. Vorhees, Washington, D. C.
B. S. Walcott, Washington, D. C.
G. H. Walker, Windsor, Ontario, Canada.
Herman B. Walker, Washington, D. C.
Percy H. Walker, Washington, D. C.
R. S. B. Wallace, Dayton, Ohio.
R. G. Waltenberg, Washington, D. C.
Dr. H. N. Warren, Salt Lake City, Utah.
R. H. White, Niagara Falls, N. Y.
W. Wilson, East Orange, N. J.
Mrs. Chas. Wirt, Philadelphia, Pa.
F. A. Wolff, Washington, D. C.
J. C. Woodruff, New York City.
Mrs. J. A. Yunck, S. Orange, N. J.
Miss Agnes Yunck, S. Orange, N. J.

MEMBERS ELECTED AND QUALIFIED.

Since Last Membership List (Dec. 31, 1915).

January	3:	F. Hurum	Pittsburgh, Pa.
"	7:	W. L. Stevens	Rancagua, Chile
"	7:	B. B. Freud	Chicago, Ill.
"	10:	P. A. Schoellkopf	Niagara Falls, N. Y.
"	10:	N. O. Williams	Jermyn, Pa.
"	10:	H. N. Gilbert	Niagara Falls, N. Y.
"	15:	C. S. Cole	San Francisco, Cal.
"	15:	W. H. Watkins	Brooklyn, N. Y.
"	19:	Chas. H. Viol	Pittsburgh, Pa.
"	19:	W. H. Carrier	Buffalo, N. Y.
"	19:	Ivar Hole	Kristianssand, Norway
"	19:	W. L. Van Keuren	North Bergen, N. J.
"	24:	F. J. Liscomb	Chicago, Ill.
"	24:	W. J. Winninghoff	Anaconda, Mont.
February	1:	N. Kameyama	Tokyo, Japan
"	1:	G. E. Weissenburger	Keokuk, Iowa
"	7:	L. B. Cherry	Kansas City, Mo.
"	7:	R. W. Hyde	Murray, Utah
"	7:	J. J. Frank	Pittsfield, Mass.
"	9:	J. H. Finney	Washington, D. C.
"	9:	D. L. Mathias	Pittsburgh, Pa.
"	14:	R. V. Townsend	Wappingers Falls, N. Y.
"	14:	B. H. Jacobson	South Bethlehem, Pa.
"	14:	Chester A. Orr	Cleveland, Ohio
"	14:	Job Fish	Buffalo, N. Y.
"	18:	T. L. B. Lyster	Niagara Falls, N. Y.
"	18:	S. E. Osborne	Niagara Falls, N. Y.
"	18:	R. Loken	Kristianssand, Norway
"	18:	Wm. J. Van Sicklen	Houston, Texas
"	18:	J. R. Moore	Oakmont, Pa.
March	1:	A. T. Baldwin	Jersey City, N. J.
"	1:	C. G. Hardie	Buffalo, N. Y.
"	1:	T. S. Olsen	Vadhein, Sogn, Norway
"	1:	Sentaro Higashi	Tajima, Japan
"	17:	J. F. Schoellkopf, Jr.	Buffalo, N. Y.
"	17:	B. H. Ritter	Niagara Falls, N. Y.
"	24:	E. Mueser	Niagara Falls, N. Y.
"	24:	W. S. Meyers	New York City
"	24:	A. B. Starr, Jr.	Pittsburgh, Pa.
"	24:	Jacob Trantin, Jr.	Chicago, Ill.
April	5:	H. Rollin	Charleston, W. Va.
"	5:	A. W. Davison	Cincinnati, Ohio
"	5:	Wm. T. Little	Massena, N. Y.
"	5:	F. J. Liscomb	Chicago, Ill.

April	5:	H. A. Harper	Rancagua, Chile
"	5:	J. G. Thompson	Ithaca, N. Y.
"	5:	G. R. Kinter	South Bethlehem, Pa.
"	5:	H. K. Moore	Berlin, N. H.
"	5:	A. C. Dalton	Quebec, Canada
"	5:	Prof. Farup	Trondhjem, Norway
"	5:	H. M. St. John	Chicago, Ill.
"	5:	H. L. Noyes	Niagara Falls, N. Y.
"	5:	J. J. Yager	Buffalo, N. Y.
"	5:	H. M. Eastman	Denver, Colo.
"	5:	I. E. Lee	Rochester, N. Y.
"	5:	L. B. Kramer	South Bethlehem, Pa.
"	5:	A. W. Whitaker, Jr.	Niagara Falls, N. Y.
"	5:	E. Tatsumi	New York City
"	5:	C. Legrand	Douglas, Ariz.
"	19:	J. L. Adams, Jr.	Wilkinsburg, Pa.
"	19:	C. T. Henderson	Milwaukee, Wis.
"	19:	G. A. Richter	Berlin, N. H.
"	19:	John Lebherz	Niagara Falls, N. Y.
"	19:	J. H. Haynes	Victor, Colo.
"	19:	R. J. McNitt	Perth Amboy, N. J.
"	19:	A. J. Helfrecht	Madison, Wis.
"	19:	C. N. Lansing	Niagara Falls, N. Y.
"	19:	F. S. Low	Madison, Wis.
"	25:	H. J. Brownlee	Toronto, Ont., Canada
May	2:	D. Miller	Rahway, N. J.
"	2:	Geo. O. Loeffler	Pittsburgh, Pa.
"	2:	L. R. Baker	Manitoba, Canada
"	2:	C. S. Redfield	Trenton, N. J.
"	25:	M. F. Thompson	Prairie Grove, Ark.
"	25:	E. K. Cooley	San Francisco, Cal.
"	25:	T. O. Kennedy	Massillon, Ohio
"	25:	R. W. Pope	Newark, N. J.

The Presidential Address, delivered at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27, 1916.

THE MODERN ENGINEER.

By Lawrence Addicks.

One of the results of the upheaval in social institutions which is in progress in one form or another throughout almost the entire civilized world, is going to be a changed attitude toward the engineering profession. Engineering—etymologically it means producing, and might today be defined as co-ordinating the forces of nature and properties of matter to the use of mankind—is one of the earliest occupations of man. Indeed much of what we call animal instinct is based upon an appreciation of engineering principles, as when an animal determines the direction of the wind from deciding which side of its damp nose is the colder from evaporation. And when we teach a boy scout to build a fire in the open without using more than two matches, we may call it wood craft, but it is a first-class laboratory experiment in engineering.

Although it deals with such fundamental principles, engineering has not been recognized as one of the great professions until well within the last century. This was doubtless due to the fact that until a clear understanding of the principles of thermodynamics and of the laws of chemistry existed, no rational development along lines of efficiency and conservation was possible, and the popular attitude was anticipated by Shakespeare when he wrote:

> "Let it work;
> For 'tis the sport, to have the engineer
> Hoist with his own petard."

The wonderful developments in engineering science in the last generation, however, have put its expositors equally on all fours, if you will pardon the expression, with those of any of the other learned professions. Still, while the accomplishments of the engineer are today admitted on all sides, he has not taken the

position in the active direction of the affairs of mankind, particularly in matters of government, which after all lie at the very root of our social welfare, that these accomplishments warrant.

The chemist appears to suffer from all the disabilities of the engineer to which are added some misfortunes all his own, which doubtless explains the uncomprehending attitude of the general public toward the chemical branch of the engineering profession. I suppose the average man, upon being put to one of those psychological tests which require an immediate and unreflecting answer to a question suddenly proposed, would state that a chemist was the British name for a drug store. One of the reasons for this is that the chemist works chiefly with raw materials which the public seldom see as such, while the engineer produces telephones and trolleys and bridges and big guns which testify at close range to his usefulness as a citizen. When we come to the electrochemist, I fear he is generally regarded as the unfortunate result of the electrical engineer having got into bad company, and the color line is apt to be drawn so as to keep the engineering blood pure and put all half-breeds in the Jim Crow car with the chemists.

Now this is all wrong. The chemist is as good a man as the electrical engineer and the electrochemist, or electrochemical engineer, as I should prefer to call him, should be a better man than either, owing to his wider technical horizon; but our congenital disabilities tend to keep us in the background, which is the reason for these few words in a sort of Booker T. Washington style as to the future of our race.

The affairs of government in this world seem to be run alternately by the soldier and the lawyer. After a war there is a strong demand for soldiers as presidents and other government officials. Then as the glamor wears off and things calm down, the lawyer, who is the original safety-first man, comes out of his hole and with his gift of speech persuades the people that laws should naturally be made by lawyers and he will just take charge. The first part of this cycle is based upon the people's admiration for the men who do things, and the soldier is well reported in the papers, and the second stands firmly upon that first principle of advertising, that if you say a thing often enough you will not only convince everyone else but you will believe it's so yourself.

In business life the situation is similar; the president of the company is almost always a lawyer or a banker while the man who makes the business worth running in the first place is the technical engineer, somewhere downstairs. This is undoubtedly due in part to the fact that, I hardly know whether to say fortunately or unfortunately, most of us have just a touch of that artistic sense which is shown by devotion to a profession for its own sake, that has always made for exploitation by the more worldly-minded and has tended to lower standards. You know what a crafty looking lot the angels of the old masters are—due to the latter finding it convenient to reproduce the features of their patrons.

The great war has brought the engineer suddenly to the front, not only of the fighting line where he shares honors with the doctor and the nurse, but of the whole complex industrial organization back of the gigantic struggle, both of the countries at war and of those neutral nations undergoing a commercial upheaval. In the fighting zone it is called a mechanical and chemical war. At home our preparedness campaign is steadily assuming shape as an organized piece of engineering, carried on by engineers, which is as it should be, and further we have the very welcome sight of the several large engineering societies acting in harmonious co-operation. At the end of the war there will be an immense amount of physical damage to be repaired which will be another great engineering undertaking. The opportunity is here, the events of the last two years having accomplished what would have required at least a generation of peaceful development.

The great question is whether the engineer will rise fully equal to his opportunity. To do this he must first of all lay aside all narrow sectarianism, the technical men in all branches realizing that they are of a common brotherhood. Then he must broaden his interests and not remain satisfied with the purely technical aspects of the problems which present themselves, but study and grasp their larger economic significance. Finally he must not rest content with acting in a merely advisory capacity in the affairs of business but have the self-confidence to see his work through from laboratory to factory, from factory to market, at home or abroad, and if necessary, from market to the economic situation beyond.

To accomplish these ends he should be not only a member, but

an active member, of some professional society. Let him belong to as many societies as he chooses, but select the most congenial and make himself in evidence at its meetings. Then collectively he should endeavor to bring the various societies together in joint meetings, committee conferences, etc., whenever possible, so that the profession may not only present a united front to the public but know its own mind on questions of general interest. Then, when engineers are in agreement on a technical question affecting public interest they should let their collective voice be heard. I believe that it is not only permissible but desirable that technical societies take an active part in legislative hearings, and offer suggestions or protests on public questions, provided only that the opinions advanced are really held by a reasonable majority of the membership, that the questions acted upon are reasonably relevant to the subjects covered by the societies' interests, and that a sharp distinction is drawn between matters of public interest and political campaigning.

In short I submit that one of the first steps toward giving the engineering profession the place in public influence it deserves should be the vitalizing of the great engineering societies as living representative bodies of engineering opinion and the education of the public and the government to look to them for advice on engineering matters.

The Naval Consulting Board is a most encouraging application of this idea and it is to be hoped that this policy will be extended to other departments of the government. Such co-operation should make it impossible for Congress to be so long in lack of reliable information on which to base an intelligent constructive policy, that this country should be in a period of military anxiety dependent upon a foreign supply of nitrate for explosives, with the only nitric acid produced from the atmosphere being that which turns the milk sour in the refrigerator when we have a thunderstorm.

Communications presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

A SYMPOSIUM UPON CO-OPERATION IN INDUSTRIAL RESEARCH.

INTRODUCTION.

By L. Addicks.

A year ago, at the meeting of this Society at Atlantic City, quite an animated discussion arose on the floor regarding alleged lack of co-operation between the "technologist and the teacher," as Dr. Bancroft puts it. The chair quite properly suppressed this line of argument as not being germane to the subject of the paper at that time under discussion.

The matter seems of sufficient interest, however, to justify a reopening of the question and the following briefs have been prepared by request for the Professional Society, the University, the Government, and the Corporation. There has been no collaboration between the various authors, a fact which increases the interest, if not the unity, of the presentation.

A fifth party at interest would be the so-called practical man in the field, but it is hoped that the audience will amply supply his point of view.

THE PROFESSIONAL SOCIETY.

By L. Addicks.

The professional society is supposed to afford a clearing house for ideas where technical or ethical matters lying within the field of the particular profession may be discussed from a purely individual point of view. Unfortunately the papers presented at meetings such as this, almost invariably deal with a successful, or at least a completed, research. We rarely receive a report

of a failure and practically never a statement of an unattacked problem. I believe that every society should have a "lion's mouth" where brief statements of lines of commercially desirable research could be dropped. These problems should be considered in our various university laboratories and the results of such consideration embodied in papers before the Society.

At present the situation seems to me to present three unrelated factors: the practical worker in the field, the so-called theoretical worker in the university, and the supposedly common meeting ground of the professional society.

The practical worker is continually running against obstacles which he seldom has the leisure, even if mental and laboratory equipment be at hand, to solve. Even the large corporations maintaining adequate research laboratories have long waiting lists of what seem at the moment to be commercially secondary problems. Every one of us can easily recall such problems in his own experience.

The university exists primarily for the education of young men and women, a purpose which is sometimes lost sight of. The laboratory exercises and thesis work required of the students, however, afford an excellent opportunity for the attack of problems having definite commercial value. The moment a student learns that the work he is engaged upon is of some immediate practical interest to the outside world, he has a much greater interest in its prosecution. Further, such a thesis gives a man sufficient special experience to make him of value after graduation and assists in obtaining a position a little above the ordinary try-out—witness, for example, the celebrated case of the secretary of this Society who has not yet been able to live down his thesis.

Now mark you, I am not suggesting taking paid work from the notoriously underpaid faculty or from the consulting engineer and substituting free student advice, worth about what it costs. The problems I have in mind are those which are not of sufficient immediate importance to bring them into the paid class and yet which under such experimentation might yield suggestive if not absolutely accurate steps toward solution. Why not work on the causes and nature of what Gore called "transfer resistance" in an electrolytic cell, for example, as a thesis subject, rather than on the effect of ultra-violet rays on the solubility of pep-

tonized manganous oxide in butyric ether, selected at random from among the unlisted items of universal law?

In short the man in practical work should report his interesting odds and ends to the professional society; the society should publish the problems so stated; the head of a university course should consider such lists in mapping out the work to be done under his direction; the results of such work should be offered to the society for publication. In many cases I believe the results would include a better job for the student when he graduated, additional consulting work offered the professor, practical help to the man in the field and an increase in the usefulness of the society.

THE PROFESSIONAL SOCIETY.

By F. A. Lidbury.

Since the Corporation, the Educational Institution, and the Government possess means and facilities for the execution of research, whereas the Professional Society lacks these, the function of the latter in any co-operative scheme for the promotion of research will evidently be confined to the fields of suggestion and co-ordination.

In regard to the former, the Society can use its machinery for the collection and publication of proposed subjects of investigation. Would it be worth while? Such precedents as are to be found in the history of our Society scarcely suggest an affirmative answer. There was the Ferro-Boron affair, for instance; and the fact that such investigations as are clearly traceable to the statements of the lacunae in our knowledge of electro-plating theory made at the joint meeting with the Electro-Platers' Society at Atlantic City have been conducted in quite different directions from those then suggested. And naturally, any competent director of investigation, either in technical or educational work, requires no external suggestions. However, as experimental evidence is the most convincing, there is no reason why the collection of suggested subjects for investigation should not be tried, even if the result were only to add to the gaiety of nations.

As regards the co-ordination of investigations in the different classes of research institutions the Society's main function is the establishment and maintenance of communication between these. Primarily this is done by its publications; but to be content with the development of publications is seriously to limit its usefulness in this direction. To foster the discussion of papers from the most diverse points of view, to attract to its meetings men engaged in different phases of scientific endeavor, and to stimulate the personal association on these occasions of men interested in electrochemical research from various angles but who would otherwise rarely if ever meet—these are some of the things which the Professional Society can do to bring about the desired co-ordination. But this is nothing more than the development of the normal activities of such a society; and my own opinion is that a society's success in the co-ordination referred to depends entirely upon its success in its own development and in the attractiveness of its meetings. In this respect the American Electrochemical Society has been most fortunate, and if it is possible for one of these gentlemen (of whom one hears but rarely finds) who are short of a subject on which to exercise their abilities for investigation to attend a meeting of this Society and not find a dozen, he has surely mistaken his vocation.

THE UNIVERSITY.

By W. D. Bancroft.

In most college laboratories the amount of power available for electrochemical work is not large and what power there is may not always be available during the night. The students, who are doing electrochemical research, work intermittently and it is only occasionally and for relatively short intervals that it is possible for them to work in successive shifts. Consequently electrochemical research at most colleges must be limited to problems calling for a moderate amount of power and for relatively short runs. Co-operation with technical men is therefore possible only for selected problems, most of which are not of much interest to the technical man. What the college can do best is to clear up the theoretical side of a problem; but if the process is actually running successfully on a commercial scale, the question of why

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it works is relatively unimportant, except in so far as it may lead to new developments. The man who patented the addition of chromate to a chloride bath had an utterly wrong idea of the way in which the chromate acted; but his patent was valid so far as I know. The college laboratory may work out the theory of addition reagents in electro-plating and the theory when developed may point to the use of better addition agents than we now have; but there is no certainty of this latter occurring.

The college laboratory may co-operate in working out better measuring instruments and better methods of measuring. Tucker showed how to measure temperature in a toy carborundum furnace. Gillett made the method applicable to a laboratory furnace, and then it was possible for Saunders to work out the conditions necessary for measuring temperatures in a commercial furnace.

There are other ways, of course, in which co-operation between the teacher and the technologist may take place; but the most serious problems which the technical man has to face are those which arise from doing things on a commercial scale and the college man cannot help in those as a teacher though he may be an expert. I think that we should keep in mind the distinction between the college professor as teacher and as expert. In so far as he is an expert there is no question of co-operation. It is a case of professional services, paid for as such and carrying with it the obligations of secrecy. The work which cannot be done in the college laboratory will be done in the technical laboratory or in the factory. In so far as the college professor is a teacher, it is obligatory on him to publish his results for the benefit of everybody. Under these conditions the possibility of co-operation is very limited and, as a matter of fact, does not occur to any appreciable extent.

I believe very strongly in the desirability of an exchange of ideas between the teacher and the technical man. I believe that it is of great value to the teacher to be interested in, and to keep in touch with, technical problems. I believe also that it is a very good thing for the technical man to know as much as possible about the theoretical side of his own specialty and of the allied subjects. I don't see any object, however, in ignoring the fact that the primary business of the college chemist is to find out why things

go as they do in a given case, whereas the primary business of the technical chemist is to find out what to do in a given case. The two should each supplement the other; but the differences in the problems themselves, the differences in the scale of the problems, and the differences in regard to publication, seem to me to make co-operation out of the question except in special cases. The industries can subsidize the college laboratories; but let us call it that and not co-operation.

THE UNIVERSITY.

By W. H. Walker.

Whether co-operation between the University and Industry be voluntary or compulsory, the results of such united effort is clearly demonstrated by the condition of industrial preparedness in which the nations of Europe found themselves at the outbreak of the present war. It is only necessary to recall the fact that but for the co-operation of Haber and Ostwald, of the University, with the manufacturers of nitric acid, Germany would long since have gone down in defeat.

Co-operation means working together for a common purpose; the combined striving of two agents for the accomplishment of a definite result. In order that co-operation may be fruitful, therefore, it is essential that the two parties to it have a clear understanding of the end towards which they strive; otherwise they may be more or less mutually helpful, but never effectively co-operative.

What then is the goal towards the attainment of which the University and Industry must strive; what result beneficial to both must be the aim of their co-operation? Clearly it is the increase of knowledge among men and the application of this knowledge to the manifold activities of men. This object is dual in its nature, but single in its method of operation if the most rapid progress is to be made, and the greatest good accomplished. In the past we have allowed ourselves to differentiate the interest which each party to the co-operation may assume. We have left it to the University to provide for the increase of knowledge and allowed it to be indifferent to the application of this knowledge. We have assumed that Industry is interested in the utilization

of knowledge, but we have placed upon it no responsibility for the "increase of knowledge and its diffusion among men." As a consequence we have had no co-operation.

This lack of united effort toward that industrial progress on which we depend for our national strength is due, in the last analysis, to selfishness. The National Government is selfish in that it takes no part in promoting co-operation between the Universities of the country and the Industries. With the exception of agriculture it renders no aid to the University which enables it in turn to aid the manufacturer.

Our university professor is too often self-centered and self-satisfied. Being a self-made man he is very proud of his creator. When he diffuses knowledge among men, he presents it to the elect and is apparently indifferent as to whether it be generally understood or applied. Force becomes work only when in motion; so are ideas of value only when put into action.

Finally, the industrialist is selfish. He hugs to himself his cherished secrets and discloses nothing. He absorbs all the knowledge he can, but reflects none. Even investigations which for his purpose have proven fruitless, he declines to publish lest some one should profit by them. He is not interested in the increase of knowledge unless he can be shown wherein he will directly benefit thereby.

Co-operation in industrial research must be based upon a realization of the fact that increase in knowledge must go hand in hand with application of knowledge; that the University must maintain an interest in the application of the laws and theories which it discovers and teaches; and finally that the industries must realize that it is their duty to increase and diffuse knowledge as well as to utilize for their own profit that already existent.

THE GOVERNMENT.

By D. A. Lyon.

One phase of Industrial Research in which the Bureau of Mines is particularly interested is that which has to do with discovering ways and means for recovering metal values from:

(1) Ores which have heretofore been considered too low grade or too complex to treat by present-day processes.

(2) Tailings dumps resulting from the treatment of non-ferrous ores by processes which yield only a comparatively low percentage of the total values contained in the ores.

This phase of the research work of the Bureau also has to do with attempting to find ways and means of preventing the losses of metals which now take place in ore dressing and metallurgical processes.

The reason why the Federal Government should interest itself in the above-named problems was well stated by the late Director of the Bureau of Mines, Dr. Joseph A. Holmes, in his third annual report. As pointed out by him, one phase of the mining industry of the greatest national concern is that which has to do with insuring a more efficient, or a less wasteful, development and use of our mineral resources. As regards this phase of the industry, and as stated by Dr. Holmes, the mineral losses are considered as national losses for the reason that the mineral products of the country, becoming articles of inter-State commerce, are used by the people of all the States quite regardless of their source. For the same reason, the cost of investigations looking to the prevention of these losses, should not fall upon any one State. If conducted by each of the States, the result would be extensive and unnecessary duplication of effort and expenditure. We cannot expect the individual operator to bear the entire cost of such investigations for the reason that ways of prevention with him are questions of temporary profits, and his temporary profits, in many cases at least, are greater by virtue of his using wasteful methods. With both the community and the nation the situation is often quite different, and they must safeguard their own permanent welfare.

For the reasons stated by Dr. Holmes, the Bureau of Mines extended its investigations as soon as its appropriations would permit, to a study of ways and means of preventing mineral waste. Inasmuch as Congress wisely prescribed that the Bureau shall not conduct investigations in behalf of private parties nor participate in the promotion of individual enterprises or properties, it may be of interest to note how the Federal Government carries on investigations along the lines above mentioned, and yet keeps within the confines prescribed by Congress. Taking for example the work of the Salt Lake station of the Bureau of

Mines, which is for the most part, co-operative. It has been developed largely as a result of the fact that in 1913 the legislature of the State of Utah provided for the establishment of a metallurgical Research Department in connection with the State School of Mines of the University of Utah. Although this act became effective in July, 1913, it was not until the latter part of January, 1914, that a working arrangement was effected with the U. S. Bureau of Mines, by which the Bureau furnishes the Director of the Research Department, and other assistants, the University of Utah providing buildings and equipment and also six "fellowships" with a yearly value of $720.00 each. The "fellowships" are awarded to the graduates of colleges and preparatory mining schools which have shown a special aptitude for research investigation.

The work of this Department of Metallurgical Research, with which the Bureau co-operates, has been conducted as follows: A preliminary survey was first made in order to obtain some idea of the location and extent of the low-grade ore deposits of the State. After having determined, as a result of this survey, the probable tonnage of these low-grade ores, samples of the same were obtained, as likewise of tailings piles and dumps. A study was then made of these samples in order to determine the chemical and physical nature of the ore bodies from which they were taken. This having been done the samples were then tested by various methods in order to find, if possible, an ore dressing or metallurgical process by which the metallic values could be feasibly and economically recovered. However in doing this work only those samples were selected which were fairly representative of a certain class of ore or tailing in each particular district. In no instance was work undertaken with the idea of working out a process for some particular ore found only on some particular property. In other words, the Department has endeavored to avoid doing work which an individual or a company should hire a metallurgist to do, as it is not within its province to do work which would be in competition with the private metallurgist or with the mining engineer. For this reason the Department does not receive ores and make tests on them for an individual or company for the sole purpose of determining what process would be most suited to the treatment of the ore of that

particular property. When such work is desired, the Department has employed such help as was necessary to do the work and has charged it to the party wishing the work done, or has permitted the party wishing the work done to do it himself, under the direction of the metallurgist in charge, it being understood that no work of this kind can be carried on in the laboratory of the Department which will not, in the estimation of those in charge, have a helpful bearing on the general research work of the Department; that is, furnish additional information as regards the solution of similar problems. Moreover, it is understood that any data or information obtained in this way shall be the property of the Department as well as of the individual or company doing the work, and can be published by either the University or the Bureau of Mines, as they deem best.

During the past year several companies and individuals have availed themselves of this opportunity.

In addition to the co-operative work which the Bureau is carrying on with the University of Utah, it has also taken up co-operative work with various other State institutions, but not on such an extensive scale as with the University of Utah. As an illustration of such co-operation, the work which is being done on flotation may be taken as an example. At the present time the instructors in mining and metallurgy in most of the mining schools of the country have become interested in the flotation process for the recovery of values now being lost in the treatment of non-ferrous ores. Inasmuch as the Bureau, in its work of the conservation of the mineral resources of the nation, attempts to keep in close touch with all important metallurgical research work in the country, it has been found that it can assist these departments of mining and metallurgy with whom it is doing co-operative work, by acting as a clearing-house of information as regards the work which is being done on flotation processes throughout the country as well as other lines of investigation which the division of metallurgy is conducting and which has for its object the prevention of mineral waste. In brief, the above is one phase of Industrial Research which the metallurgical division of the Bureau of Mines is carrying on at the present time, and which has been found to work most satisfactorily.

THE CORPORATION.

By L. H. Baekeland.

It is almost self-evident that under certain conditions, co-operation in electrochemical research may bring about greater efficiency and quicker results at less expense and less effort. Unfortunately, such a co-operation is frequently difficult if you take into consideration that private corporations, for obvious reasons, do not desire to acquaint others with their particular needs, their technical weaknesses, or their future plans. Most of the time, also, research is closely interwoven with the delicate subject of patents.

Then again, in order to understand a fully desirable subject of research, it is often necessary to know, in detail, the other ramifications of a technical problem. It is not always an easy matter for an outsider to get acquainted with the full scope of such a problem unless he has acquired practical experience in the subject.

All these considerations and many others have been the guiding motive whenever large chemical or electrical corporations have seen it to their advantage of organizing well-equipped research laboratories where they tried to solve their own problems, independently of any outside intervention.

It is true that the running of such large laboratories involves considerable expense. Nor is it simply a matter of expense; it requires the proper man to be at the head of such a research laboratory, and men with the necessary qualifications for this kind of work are few and far between. It is easy enough to vote a credit for a research laboratory, but the real difficulty is to locate the proper men who will use the appropriation to good advantage.

All these considerations seem to point to the fact that in many cases, co-operation in research would be the most practical plan. For instance, several concerns interested in the same problems might co-operate together for maintaining a joint research laboratory, or for entrusting a specific problem of research to a man or a group of men who possess the necessary qualifications. That such a plan is possible and profitable, is best illustrated by the well-organized research laboratory of the National Canners' Association, of Washington, at the head of which is Dr. W. D. Bige-

low, formerly of the Bureau of Chemistry, and which I believe is a unique institution of the kind in the world.

Why could a similar co-operative research laboratory not be organized for the study of problems of electrochemistry?

THE CORPORATION.

By W. R. Whitney.

Successful corporations are usually guided by broad-minded men. In general, the broader the field of the industry, and the greater its activity in that field, the wider will be the horizon and interests of its directing forces. Therefore there is usually in them what the engineer calls a torque, tending to contribute to the scientific research of the country. This torque is apt to be limited by the restricted vision of the narrow specialists or the direct agents for research, rather than by the directors of the corporation. This is due to the lesser knowledge of the affairs of men possessed by the research specialist, who naturally confines his study more to things than to people.

Just as no man liveth unto himself alone, so no scientific research is separable from the rest of knowledge, and for this reason the greatest value of research will be realized where there is the widest range of utility and interest. The researches of a Mendel, buried in a monastery garden, or of a Gibbs, buried in a "Connecticut Transactions," come to light all too tardily. The applications of these two researches, for example, after years of hiding, now influence the laboratories, the factories, and the farms of the world. But one-man laboratories and one-horse publications fail to fulfil the possibilities of their discoveries because of isolation from the fields of need.

A large corporation can better afford to carry on extended research than a small one. A company which sells only a few hundred dollars' worth of material a day can ill afford to risk one hundred dollars per day on researches to improve that particular product. Were the manufactured product of a company infinitely varied or extended, then the utility of newly discovered facts

might have infinite application. This condition is actually approached as the breadth of interests of a corporation increases. An isolated iron foundry can hardly undertake research on X-rays and colloids, on magnetism and sanitation, on optics and ionization. But the iron foundry may be benefited by any of these. It is so also with personnel. No one head contains all the useful knowledge of the world today, as may possibly have been the case when Babylon fell or St. Peter's rose. Therefore the association of research workers in the laboratory of a corporation ought to increase the useful yield over that of an equal number of isolated men. The effect of co-operation is not merely additive, but rises more nearly as the "n"th power, where "n" is the number of co-operators. And so I am led to regret that large corporations have been so frowned upon. Some time we may realize that at least in so far as research is concerned, it were better if all our productive organizations were united, with a single great research laboratory. Then the poorest furnace slag would be quickly tried for farm fertilizer, tested in cements, made into glass, ground into paints, calendered into writing paper, blown into thermal insulation, turned into asbestos, put into dynamite, or injected into medicines. Every electrochemist who, fraternizing with his own fad, listens to a brother chemist riding his particular hobby, hears the call of co-operation. Men and experiences dovetail, and in the words of the dictionary definition, "Each finds in the other what he in a double sense wants."

The desirable degree of co-operation in research between the different existing laboratories can hardly be brought about by any of them as now constituted. The industries, under pressure for time, tend to myopic research. Business expediency enforces secrecy that competitors shall not share the results without sharing the expense, consequently there is duplication of work.

The universities are, properly, so far out of touch with technical practice that they do not realize the needs of industry and not infrequently choose untimely researches, or their discoveries fail to receive application where most needed.

The work of the Government bureaus is often neglected by the business concerns which might develop the processes but fear to do so in the absence of patent protection.

The plans for a Government research laboratory for the Navy

naturally led to the question of turning to account in some way the facilities of private, corporate and university laboratories. Here for the first time a proposal of general co-operation in American research seems practicable. Within the organization of a Government laboratory might be one or more official co-operators. His duty would be to familiarize himself with the needs of problems of the country, the facilities of all the possible research laboratories and the idiosyncrasies of the individual in them. He would inform the latter how he might co-operate, would follow his progress and keep him generally informed. Such a Government employee would be more likely to meet liberal co-operation than would a representative of a university, or of any private or corporate interest. This official would become a traveling encyclopedia. Such a procedure in conjunction with the normal work of a governmental defence laboratory might indicate by experiment what the next best step along this line of co-operation should be.

DISCUSSION.

W. H. Walker: Dr. Butler in an address stated that co-operation can either be voluntary or compulsory, and he pointed out that in Germany, in a State where it is compulsory, the universities do get co-operation from the manufacturing establishments, and the result is what we have observed. That kind of compulsory co-operation we cannot have in America; it must be voluntary in order that we may reach the highest good. I may be idealistic in my third paragraph, in which I point out that co-operation must in the end be general in the case of people striving for the same end, each one contributing something and each one getting something. Co-operation in the past has been too much of the kind where one fellow gives something and another fellow wants it all.

In the American Society for Testing Materials' Committee on Preservating Coatings, we recently had a discussion of paints. The paint manufacturers pointed out how many problems there were which should be solved by physico-chemical study of paints,

pigments and oils. The people who thought they knew something about physical chemistry commenced to ask questions relative to the problems, and the paint manufacturer said, "Come to my factory and I will show you what I mean." I believe that is going to be the true spirit of what I call co-operation. If the paint manufacturers will take the physical chemist and show him what they mean, they will awaken his interest. If the paint manufacturers insist that whatever is introduced in the way of improvements is their own property, and keep it to themselves and use it in their factories, that is not co-operation in the broad sense. This information must be disseminated to make it of the greatest value. It may, on the other hand, help the particular individual a little bit, but it will not help them the same as if the whole trade was taken into the confidence of those who have made the investigations, and then, not only would they prosper thereby, but the whole industry and community could prosper. I have pointed out that selfishness is really the root of that, and that the Government is selfish because it will support only one kind of equipment in the Bureau of Standards and Bureau of Mines. The Government itself subsidizes a university, to the end that the university may help agriculture, but it does practically nothing to help any university that it may help its professors help the industries, and the Government can do a great deal in that direction if it sees fit to do so. That is a leaf out of the experience of Germany which our Government could study with great advantage.

Dr. Baekeland pointed out to me yesterday that the university professor did not know enough to be helpful in co-operation with the manufacturer. That may be true, but he is willing to learn, and if the professor of the university can be given a little more leisure by the governing bodies of the university, there is much that can be done. One difficulty in New England is that some of our professors take no interest in industrial affairs; they attend the meetings of the National Academy of Science with a religious fervor, and believe that when that is done their whole duty is accomplished. They do not think there is anything in an organization like ours to interest them, and that attitude is partly due to mistake and partly to ignorance, because they do not know how much they really can help. The manufacturer is not interested

in anything that you cannot show him is going to immediately benefit him. That is a narrow point of view, and on that basis we cannot make progress. I know we can be helpful, because our progress is very marked. Manufacturers are becoming more and more interested in co-operation and feel that there is more to be done and more to be learned that is helpful to the industry and to the whole manufacturing community.

My paper, as a whole, may have seemed to be a little bit destructively critical, but I did not wish it to be such. The conclusion is that we are making progress, but that we must keep it up. The people and the universities must bring influence to bear on the president and board of trustees of the universities so that they may have more leisure to devote to this sort of thing, and the technical men must bring their influence to bear on the board of trustees to have them realize that there are many ways in which they can help by bringing the matter to the attention of the universities.

President Addicks: I consider this is one of the most important items of business on our program, although not technical in character, and that is the reason I have taken the time to have it read in extenso.

As I was limited in my assignment in what I could say, I want to make a few remarks covering the discussions as a whole. Two of my examples are rather anticipated by the program itself. I waited for some years to find out certain facts about transfer of resistance, and here we have a whole session devoted to practically that subject. There seems to be some sort of telepathic influence at work. I deplored the fact that we had no unsolved problems presented, and I find we have a paper on our program entitled "Some Unsolved Problems of the Electroplater," which is to be presented at our session on Saturday, so I am, to a certain extent, answered in advance in regard to these particular instances.

I think the whole state of affairs in regard to co-operation is —one word expresses it—"rotten." The universities admit it. We have two university papers here; to be sure, one deplores it and the other glories in it, but still they both admit the fact. If you stop to consider, you will recall how few of the great useful inventions have come from our institutions of learning, where it

would seem, in the nature of things, many inventions should originate. Most of the inventions which are used come from people who have either discovered them by chance or have worked systematically with a definite purpose and object in view.

These research laboratories that have been such marked successes in the hands of some of our large companies, it seems to me, are evidences of failing on the part of the universities to make good in that line. It shows what can be done. I do not say that the blame lies with the universities, but only state the fact. I think that the blame is as much with the people on the outside who are running the practical processes, and that it is pretty evenly divided. I believe that one of the chief troubles is a lack of frankness amongst us. We are ashamed of our own limitations. The practical man, when he goes to the meetings of a society, and gets up to discuss papers, is soon conscious of the fact that he has forgotten, if ever he knew, what the chemical symbol for caffeine is. On the other hand, it is a notorious fact among manufacturers, who are versed in the practical side of the business, that our learned friends ask fool questions when taken through manufacturing plants.

If we admit our shortcomings, and get together on the basis of ignorance, rather than superiority, we will make a large step forward. It is surprising how little some of us know of the practical side of our business. I remember my personal experience when I was injected into electrolytic matters, sixteen years ago, when I was turned loose into an electrolytic refinery. I was there as an electrical engineer. We were consumers of power, and the first problem I took up was to discover where our power went, and whether anything could be done to diminish the consumption. The first thing I wanted to know was whether Ohm's law applied to an electrolyte, and no one knew. There were seven hundred men in the outfit, running an electrolytic process, and not one knew whether Ohm's law applied to electrolytes. I found that out without great difficulty from text-books, and the next thing I wanted to know was what the composition of an electrolyte had to do with resistance. I hunted in the various text-books without finding much. Most of the available books were British and you know what an English text-book is. The back falls off the first time you open it and the index somehow failed to hatch out prop-

erly, and you hunt vainly for specific statements instead of generalities. As I remember, I found the nearest approach to what I wanted in Whetham's "Solutions and Electrolysis," which contained pages of tables, all printed with a view of proving this or that about the dissociation theory, but no one could find any trace of any practical electrolyte or anything approximating to it.

Then I next ran across the question of transfer resistance. I did not know what it was, but I found accidentally it was there. I could find nothing out about it, beyond a reference in Core's works. I brought the matter up at once of these meetings, and no one knew anything about it, and until this present set of papers was put out there was no published information I could discover about it. And today this has not come from a practical reason, but because you are interested in adsorption and its effects, which might have been found out twenty years ago, saving money in the meantime.

I think the trouble, of course, lies in the fact that the men at the top of the industries, who are in charge, have been ultra-practical men, who believe that the professor in the university is absolutely unpractical, and that there is no use in talking to him. Until we get real engineers in charge of these industries, I think it is up to the universities, first, to make a showing. You know they are supposed to be the men with the greater intelligence, and you assume that men in the universities should be willing to meet the less intelligent men more than half way, and if the university man would step out and solve some of these practical problems, of course, he should be paid, there would be a change of heart on the part of those running the industries, and a great change of income on the part of the professors.

F. A. J. FitzGerald: One of the first things necessary for successful co-operation is an undivided desire for it. This is lamentably absent in many cases.

I do not believe that a mere statement of problems at meetings of a professional society is going to encourage anyone to take them up. It is interesting to have these problems stated at meetings, but I doubt if many people would take them up, and if they did it would result in an undesirable duplication of work.

If the technical man wants the college professor to take an

interest in any problem he will have to talk to him personally and if possible get him to come and see his works, as was suggested by Dr. Walker. But then would it not really be better for the technical man to employ chemists to work on these problems for him, rather than go to a college or several colleges in the hope that some of them will find out something he wants?

How far colleges can work on technical problems is another question. If they devote their time nearly exclusively to technical problems there is apt to be neglect of training students in fundamental principles. What is greatly needed in colleges is a closer attention to fundamental principles in their relation to practical problems. I have had a good many men who worked for or with me who were so keen on practical problems that they paid very little attention to fundamentals of chemistry and physics, and that is where they fail when they come to the study of practical problems. As to what the professional society can do, if personal communication between the college professor and the technical man is as desirable as I believe it is, then the meetings of the society should be so arranged as to give as much opportunity as possible for ordinary conversation and perhaps somewhat less devoted to papers and their formal discussion.

C. E. Skinner: The view point of any one who discusses the question of co-operation in industrial research will usually depend on whether he represents the Government, a corporation, or a technical university, and careful reading of the briefs which have been so ably presented shows that the individual experience of those who have discussed the subject has been the governing factor in bringing about their particular points of view.

One main idea, however, seems to stand forth in these briefs, and that is that co-operation is desirable, but those who have had the most experience, particularly in corporation work, see many obstacles in the way of complete and cordial co-operation, particularly where the desirability of patent control plays a part.

It has been the writer's good fortune during the last year to come in contact with some of the men who are most profoundly concerned in Great Britain, at this time, with regard to the future of research in that country. Some very able men interested in this subject have visited many of the corporation, university, and

research laboratories in this country, and have carried back with them the impression that an enormous amount of work is being done in America, but that there is little co-ordination or co-operation between the various interests involved. They seem to feel, as I understand it, that in Great Britain conditions are such that it will be impossible for either the industries or the universities to individually make substantial progress during the reconstruction period which must follow the war, and they feel that some system of co-operation must be worked out if the best interests of all are to be served. It is possible, therefore, that Great Britain may, through her necessity, point the way for such co-operation to us who are at this time in a better position, both in our schools and in our corporations, to carry on individual researches, even though the work may be duplicated in many places.

In Great Britain the average corporation is relatively small, competition has been exceedingly keen, both from internal and external sources, and the tendency has been apparently to eliminate all matters of expense which were not immediately justified. In this country, the average corporation is much larger and has, of recent years, in the main been prosperous and therefore in a position to spend money for research which would benefit the corporation and which would not be available to its competitors.

A plan is now being agitated in Great Britain which contemplates a central research corporation with both the Government and the industry as contributors, with the research workers drawn from the universities and the industry, the research corporation taking out patents on all inventions and discoveries, with the scheme of licensing any corporation or individual who desires to avail himself of such patent control. This would also involve an exchange of workers between the universities and the research corporation. While there are undoubtedly many obstacles to be overcome, the general scheme has much to commend it, particularly under the circumstances facing its promoters.

Many of our technical universities have been growing at a rapid rate, and some of them have ample funds to establish engineering and research laboratories. As a result, we see in this country a very large number of independent units doing experimental and research work, each with the object of benefiting its own imme-

diate supporters. The Government, on the other hand, has made a splendid start in its Bureau of Standards, Bureau of Mines, Forest Products Laboratories, etc., in research work of a type which will benefit all alike. The research work done in many of the universities has mainly been in the domain of pure science, and much of it, while interesting to the scientists, is apparently of little or no immediate value in connection with industry.

The writer has found, in visiting quite a number of the more prominent universities during the last few months, that men doing experimental and research work in the schools are exceedingly anxious to attack problems which will have a distinct value in connection with the industries of the country; but they lack, first, a knowledge of what these problems are, and second, the necessary information as to the mass of correlated matter which must be available to them if their researches are to be efficient and the results of value. Many requests have been received for thesis subjects which could be worked out in connection with the problems of the corporations.

In a very large measure, the business of most of the large manufacturing corporations of this country is based on patents, and as this protection is somewhat precarious at best, the corporation cannot very well give out problems and information in connection therewith, which if not controlled, will be to their commercial disadvantage. The corporation spending large sums of money for research and development may, if such matters are not protected, find that a small competitor, taking advantage of the lack of protection, may market some product at a distinct advantage over the corporation which developed it, as it has no overhead in the way of research and development to account for. As a consequence, when such research problems are turned over to the university by the corporation, these problems must be of such a nature that any work done and results published will be of value to all and of no disadvantage to the corporation. There are many problems of this kind, and in the main they consist of the development of testing methods, the obtaining of exact data with regard to the qualities of materials, the checking of laws, etc.

Such problems, however, are not nearly so attractive to the average worker as those of the type in which the individual worker sees possibilities of making new discoveries or of develop-

ing patentable material or processes. This most attractive type of problem is therefore the one which the corporation usually feels that it must control and must therefore either carry out the work on its own premises with its own force, or it must put the workers at the university under some obligation such that the results can be controlled, if desired, by the corporation. In some institutions, particularly State institutions, such control and use of the university facilities are not allowable. I believe that much more can be done towards co-operation than has been done, but that the corporation must retain its own research laboratory entirely under control, so that it can give out its results freely or not, as it finds expedient.

William Parker Cutter: I wish to speak rather on the co-operation which exists than on a plan for future co-operation. The three societies in the Engineering Societies Building in New York City, the American Institute of Mining Engineers, the American Society of Mechanical Engineers and the American Institute of Electrical Engineers, have a large engineering library, a library of general technology covering chemistry, as well as other branches of engineering. It is the desire of those societies to make that library very useful, not only to people in New York City, but to people all over the civilized world, and in order to do that it has developed a "Service Bureau," so-called, by which any person can write from anywhere and get information, so far as it is printed, on any subject in the line of engineering work covered by the books and periodicals in the library.

I have brought several folders showing what is proposed to be done and what is being done, and call your special attention to the little map on the inside of the folder. Every dot on that map represents a town from which inquiries have come to the library. There are two hundred and fifty-nine of them, and every State in the Union, except three, is represented, and in addition to that we have inquiries from seventeen different foreign countries. The subjects at present are largely chemical and electrochemical, as would be expected in connection with developments on account of war. For instance, I might mention that we have a very long research list, with abstracts, on electrolytic zinc, one of the questions to be presented to you; on aluminium, especially its electrical

production, etc., and we would be glad to have you take copies of these circulars and learn something of what is being done in the way of co-operation between societies, manufacturers and universities, through the literature. The idea is that the manufacturer, or the university, or the society, or the Government, should apply to the library of the engineering societies for information in the literature on any subject affiliated with engineering topics.

J. J. Carty (President, American Institute of Electrical Engineers): I am very glad indeed, to have the honor of saying a word before electrochemists on this subject of co-operation. I think the friendly co-operative work that had been done between the American Institute of Electrical Engineers and your young and vigorous society is an example of how we can conduct together the different parts of the work which are assigned to us. The electrical engineers must furnish for you, in some way or other, cheap power, and the apparatus and mechanism that goes with it, and then the utilization of that power, in applying it to chemical problems, is taken up by you.

We have heretofore had joint meetings with your society. We were favored yesterday by a large attendance of the members of your society at our meeting, and our discussion was very greatly enriched by the participation of your members. I am very glad, indeed, that we are able to testify by our presence here today our very great appreciation of your help and of the valuable work that you are doing. A number of our past-presidents, some of our most important members, are here, and I know that they will be much edified and instructed in listening to your proceedings.

Carl Hering: I am very glad to see that this spirit of co-operation is developing, because it seems to me that it is the solution of many problems. We cannot possibly accomplish by ourselves all what we can if we have friendly associations with our colleagues. An interchange of ideas often leads to something that neither party had thought of.

We saw in the session yesterday, and we are seeing in our sessions of this convention, the importance of the co-operation of these two societies, the organization which Mr. Carty represents and our own. There are a lot of water-powers going to waste,

and there are many electrochemical processes which are not productive because power is not cheap enough. Hence both of them are, so to speak, idle and unproductive, while a proper combination of the two would lead to good results and profit.

One of the laws of finance is that the greater the risk of an investment of capital the greater must be the returns, or else the capital cannot be secured. But the other form of this statement is equally true, namely that the more secure the investment the lower the interest, and if therefore the interest on the capital invested in the waterpower itself can be made a first lien on the total returns, thereby virtually guaranteeing it, and securing this capital itself by the value of the total plant, the interest on this capital could be very low, thereby making the cost of the power low, which in turn makes it possible to use it for certain industries which become practicable only when the power is cheap. The speculative profits are then placed where they belong, in the speculative part of the combination. As the electric power could be used for many other purposes, it has a sure market and its production is therefore not of a speculative character like an electrochemical process is that may be in competition with other processes and may be dependent on the market for its products, on the tariff, etc.

The idea suggested in Mr. Skinner's communication, which has been carried out or approved in England, appeals to me as a very good one. I refer to the general co-operation for solving the patent question, by a joint owner licensing various corporations. Each license would then strive to turn out the best product under the same patent right; that would bring about a competition which is likely to lead to good results and avoid much patent litigation.

I think there is no question that degenerative tendencies can be discovered today in all of the classes of institutions mentioned in the symposium. We find, for instance, and it is particularly noticeable, the university trying to do technical work. We also find, in not so many instances, but the instances that we have are remarkable, that corporations are trying to do university work, particularly in molecular physics. We find the Government aping the functions of both industrial and university institutions. I do not say that conditions have not been such as to call for this kind of thing. They have, to some extent. Each of the two branches,

at any rate, the corporations and the universities, have been lax in their own particular line. The corporations have not done enough industrial research work and the universities have not done enough of pure research work, and consequently there has been a need felt in certain quarters on each side for more than has been done in the opposite direction, and instead of the proper people tackling it, the other people took it up. I cannot regard that as anything but a sign of degeneration, and I cannot call anything which will assist tendencies of that kind co-operation.

As I tried to bring out in my paper, all of the institutions involved can best co-operate with one another by means of self development. The university can do its part by cultivating pure research. As Dr. Bancroft so clearly brought out, the function of the university is to attack problems and see "Why"? The corporations can do their part by cultivating the field of research, and they should not go whining around to the professors to help them out when they get into a hole. As a matter of fact, this is altogether not a question of co-operation but of the right kind of spirit in each institution. So far as industrial work is concerned, what is needed is not so much an application to the industries of the results of university work as the cultivation of a spirit of research in industrial application, in the industrial institutions themselves. It is not a question of facilities, or the amount of money that is spent. It is largely a question of the spirit in which problems that come up every day are tackled—whether they are approached from a purely empirical point of view, or whether those whose business it is to tackle them bear in mind their relation not only to their problems but also to general scientific thought and the general state of scientific discovery.

In short, as Mr. FitzGerald indicated, the best co-operation that the universities can give to the industries is to supply them with men who are so thoroughly imbued with the spirit of scientific investigation and of such scientific and inquiring turn of mind that those industries will, through the adsorption of such men, though in a different field of endeavor, acquire that spirit themselves.

President Addicks: Of course, there is one thing about the spirit which Mr. Lidbury speaks about, and that is that some of us

seem to think that spirits improve with age when kept in bottles. I think if we could bring the spirits together on both sides of this important proposition, and get more papers like Mr. Hogaboom's paper on "Some Unsolved Problems of the Electroplater," we would make great advances.

J. W. RICHARDS: I think our corporations largely miss the fundamental facts involved when they look to the universities for solving their technical problems. As Mr. Lidbury has so ably stated and Mr. FitzGerald also mentioned, the best co-operation which the university can give the industries is to properly prepare the men.

Speaking from the university standpoint, its work is to ground the men in the fundamentals, and we must employ, and should employ, those methods of instruction which are the most effective and educative. From quite a long experience with students and teaching, I think that the so-called practical problems which come before the workers in practise possess very little educative value for the student: They are above his ability, he is not able to tackle them, does not know enough about the fundamentals. One of the great failings of our technical schools, in my opinion, is that they too quickly allow the men rein to indulge their wish to take up some practical problem, and allow them to take up questions which are very complex, possess too many variables, require an extreme amount of work, and which, in their essentials, are only weakly educative. I ask my students in my laboratory to rehearse the fundamental principles backward and forward, and the so-called practical problems of outside work, as above described, I do not care much about. I am preparing the men to be most useful to the industries when they leave me, and thorough education in the fundamentals is by far the best service which the university can do for the corporation.

How can the corporations co-operate with the university? They require these technical men. I receive probably two or three letters a week, asking me for technically trained men to go into the industries. We do not have them. The demand is several times the supply. The best way in which the industries can get the best value from the universities is to increase the facilities of the university for teaching students. We have already some very

good examples of men who have acquired wealth in the industries putting up fine university laboratories, with the object of increasing the number of technically trained men for the professions. That, to my mind, is the best way in which the industries can help the universities, and at the same time help themselves. The corporations themselves, instead of doing it by individuals, might unite in endowing the laboratories of their State or local universities, in order that the men in their State would be educated in the lines in which they most want them, so that they would have a larger field to draw upon for technically educated men.

Take, for example, the case of the metal smelters in Utah. If they would increase the facilities of the State University in Utah, so that they could get a larger and better supply of technically trained men, they would be helping themselves in a far more effective way than they can ever do by asking the universities to solve their problems for them.

W. D. Bancroft: I do not know how we are going to get anywhere in a symposium of this sort unless we can agree on some compromise. So far we cannot. Mr. Addicks points out, very truly, that the universities are not turning out large numbers of improved inventions, and he holds that up against the university. I think that he is all wrong in that respect. The great inventor does not belong in the university, it is an entirely different brand of crank that we want. Mr. Addicks also said that the universities have been making conductivity measurements on dilute solutions instead of upon commercial copper sulphate solutions. He thinks that is a pity. I think it is much better it should be as it has been. We have worked out something in regard to the theory of electrolytic dissociation, while Mr. Addicks himself could have measured the conductivity of his own solution and got exactly what he wanted in much less time than it took him to look the thing up in the literature.

Mr. Addicks also pointed out that if the university professors went into technical work more their incomes would be increased, and he seems to think that is a good thing. It is true their incomes would be increased, but I am sorry that it is necessary to do that; it is really not a good thing, but it is a choice of two evils, and the university professor should not have to supplement his income

by consulting work. So, as I see, there is absolutely no point at which Mr. Addicks and I can get together to start with.

F. C. Frary: This is a subject in which I have been interested for a good many years, and I have seen something of both sides of it. It is interesting in the discussion today to notice that all who have talked about co-operation seem to assume that it was to be between the universities on the one hand and multi-millionaire corporations on the other. It seems to me that if there is to be any co-operation, this is the kind least desired. If co-operation between the universities and manufacturers is to be valuable it will be between the universities and small manufacturers, who cannot afford to add a cost of $100 for research work to every $1,000 worth of material sold. The universities could well be of service to such manufacturers. There are multitudes of them doing the same old thing in the same old rule-of-thumb way; a few timely experiments in the laboratory in connection with this work, and a little supervision of the work in some plant, might lead to results generally useful.

From the university standpoint, there are perhaps some factors which men outside a university do not appreciate, and the first is the inherent lack of practical experience on the part of the man in the university. If he is going to get anywhere in the university, he has no time to go out and spend a couple of years in a works, even if he could get the kind of a job which would give him the desired experience. He must put in his intensive study in various lines of "higher research," as it is called, in order to get his advanced degrees and the experience which will enable him to secure a teaching position which will keep the wolf from the door. If you consider the matter from an industrial viewpoint, as to practical information, I think you will find that outside of those engaged in teaching what is known as industrial chemistry the average number of plants visited per professor per period of five years will be somewhere in the decimals. A man who seldom gets within three or four blocks of a plant cannot be expected to have the industrial viewpoint. He does not know anything about costs. You cannot expect to be able to convince him of the practical difference between doing a thing one way or another, and he cannot be expected to be familiar with the economic principles which

apply in industrial work. If he tries to visit industrial plants he is not likely to meet with general success, either. It is generally true that the industrial men keep their information to themselves, and then wonder why the professors know so little about these subjects, and ask such foolish questions. If a college man wants to investigate an industrial subject he looks around, and perhaps finds information published by some German, who told all about practice as it was twenty years before his time. If he tries to correlate his problem with present-day practice he cannot find the data, and if he is to get useful results he must repeat at his own expense of time and money much of the development work already done by the industrial plants. When the work is done, being uncertain of his deductions about works practice he does not know whether he has anything of value or not.

Most professors do not have much connected time for research work. They are continually interrupted by calls from students and by classes, meetings, etc. In general such things take precedence over and interrupt research, and tend to make it fragmentary. The difficulty of carrying on industrial research under such conditions is obvious.

Another factor which is not considered by outsiders is the matter of politics. Some one spoke of the activity of the Government in regard to agriculture. As you know, the great majority of the voters in the United States are farmers. If you can do something to help the farmer you get his vote; and that is the big argument with a politician if you want money from him, or if you wish to secure legislation. Most of the universities are dependent on legislative appropriations. The farmers look with interest on anything which is for their benefit, and with distrust on anything which tends to the benefit of the "predatory corporations," etc., or even of the small manufacturers.

The university authorities must consider where they will get the money with which to pay expenses, and if the type of co-operative research work which will be of use to the manufacturers is likely to result in cutting down their appropriations, it becomes a real danger which is perhaps not often appreciated by outsiders.

Another thing which must be considered is, as has been pointed out, the pressure on a university man to do research work and publish something, so as to make himself known outside of the

university. In many places the chief hope of an instructor for promotion and the securing of sufficient income to keep the wolf from the door is to become known outside of his university for his research work, and thus get a call elsewhere. You cannot do research work and publish it without expending time and money; the university man must live, and where is he to get the money and the time with which to do this research work, and yet live?

I take issue with Prof. Richards in regard to the educational value of practical problems. I am a firm believer in a thorough training in the fundamentals of all kinds of chemistry, but in many cases we come to a point where the student in the senior year has some time and tries to do research work. He has eight hours a week, perhaps, during which time, under the guidance of some instructor, he is trying to make a hole in the mine of unknown facts which we have before us. If he could get a little problem which had practical importance, an analytical method of interest to some branch of the industries, or some detail of a process where he could get from the literature the necessary information that would not injure anybody, and if he knew that it might be worth while after he was through, he would more frequently do something of real value to himself and other people. That is sometimes possible, but oftener it is not. Therefore we see a long list of papers published in the journals; some of them are of extreme theoretical importance, but most of them of no value at all, so far as technical chemistry is concerned.

President Addicks: Prof. Frary spent a number of years guiding youth in one of our large universities, and since that time has gone out into industrial work. I consider his remarks as an example of the rationalizing influence of industrial activities on a professor when he has escaped from the degeneracy of the university atmosphere.

S. L. Goodale: It seems to me that this discussion has been somewhat one-sided, indicating a general opinion that the industrial workers get most of the benefit of the co-operation between the university and industry. I wish to say a few words to emphasize strongly the great value to the university which results from the professors, at least those in the departments of engineering and other practical lines, themselves going out into industrial con-

sulting work occasionally, and perhaps even regularly for a part of their time. I believe the students derive a great deal of benefit from the professors' getting out into commercial work in a research or consulting capacity. The tendency of such work is strongly to hold an instructor to a kind of rationality in teaching, to help him place the emphasis where it belongs, and to keep him from wandering away from the subject he is supposed to teach, the last being a too common fault. The work is thus held to the things that are going to be of real importance. The assignment of certain parts of a real industrial research study to individual students in their senior year can be done in such a way as to arouse their interest more than almost any other means, in studies which will necessarily emphasize, as Prof. Richards has so well said, the fundamentals; and this will give tone and point to the student's work, and he will work two or three times as hard on something if he thinks it has some direct practical application in the line he is going into.

I fear it often happens that teachers, liking to ride their hobbies as well as many other people do, get carried astray from the line they are really supposed to teach and take too much of the students' time on a speciality into which they have delved deeply and which may not have much bearing on the general training the student should be getting. And it seems to me that the teacher who is spending a part of his time on real problems of commercial importance in his line of work is thus held strongly in his teaching towards the things of real importance. He is kept in touch with current developments more effectively than without such connections, and he can bring back the value of this to his students.

We have at the University of Pittsburgh the unique but highly successful Mellon Institute of Industrial Research, an endowed institution devoted to co-operation between science and industry through the medium of industrial fellowship in chemistry. At the present time there are 37 of these fellowships in operation, and 65 trained research chemists are at work in the $350,000 home of the institute. Then, too, the School of Chemistry of the university is built up around the experts engaged in research at the Mellon Institute, which also maintains a department of research in pure chemistry and a school of specific industries for the training of original investigators and technologists respectively.

R. H. WHITE: There is one point on which I think we can all get together, and that is the importance of attending the meetings of our Society; not only those sessions given over to reading and the discussion of papers but the social sessions, formal and informal, where those interested in different lines of work get together for discussion of mutual problems. This is directly in line with Mr. FitzGerald's remarks, and it seems to me that there is value in this kind of co-operation not only for those interested in industrial work but for the college professor and his assistants, and for that matter, for the society as a whole. The point I am trying to bring out is that attendance at meetings is of value not only to the corporation but to the college, and that co-operation to a greater extent will follow the clearer understanding of each other's problems, which, I take it, is the primary idea of this morning's symposium.

JASPER WHITING: It is generally admitted, both by the enlightened teacher and the progressive manufacturer, that a closer relationship than exists at present between the university and industry is desirable from many standpoints. Seldom, however, does either group take the initiative in attempting to bring this about. A kind of deadlock apparently exists, caused, possibly, on the one hand by a certain intangible, unexpressed and undefined distrust, or rather lack of trust, on the part of industry in the ability of the university to understand and solve its concrete needs; and, on the other hand, in a kind of diffidence on the part of the university—a difference created through fear that contact with the so-called practical world, and especially with the political world, might tend to smirch its character and injure its reputation in its chief sphere of usefulness—teaching.

How can this distrust, this diffidence, be overcome? Any plan that tends to make the university better known to industry, and *vice versa,* should have a beneficial effect. The professional society aims to accomplish this to a limited extent, but its chief interests lie elsewhere and it cannot, therefore, be depended upon to accomplish much in this direction. What is needed in this case would appear to be the action of a body of men with interests common both to industry and to the university and so organized as to be able to make effective their collective desires.

Such a body of men exists in the alumni of the various universities; their knowledge of the needs of industry, their acquaintance with the equipment of the university, and their sympathetic attitude toward both, vitalized and co-ordinated through their associations, should well qualify them to approach with confidence a serious study of this important problem.

In one instance, at least, alumni have already made studies of certain phases of this problem. In a report dated June, 1914, and entitled "Organized Co-operation between the Massachusetts Institute of Technology and the Commonwealth of Massachusetts," a committee of the Alumni Council of the Institute of Technology outlined the results of an extended study upon this subject. This report, which has been universally commended for its thoroughness by those who have read it, points out ways and means by which the State of Massachusetts and the industries of the State may utilize the equipment, in men and machinery not only of the Institute of Technology but of all the educational institutions of Massachusetts, to conduct research, to study the needs of the community, and to aid the State in the administration of affairs.

Of course the recommendations of the above committee would not necessarily fit conditions of other localities, and this report is mentioned here merely as an evidence of the activity of the alumni of technology, and to point out the availability of similar bodies for solving problems which have to do jointly with the university and industry.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, held at Washington, D. C., April 27-29, 1916.

NIAGARA FALLS POWER AND AMERICAN INDUSTRIES.

I. THE POWER DEVELOPMENT.

By I. R. Edmands.

There are a great many people in the United States who believe that the scenic grandeur of Niagara Falls has been seriously impaired or entirely ruined by the diversion of water for power developments adjacent to the Falls, and many of these people have loudly denounced the power companies, the users of power and even the Government, without taking the trouble to investigate the truth of their statements.

We wish to present some of the facts pertaining to the use of water for the development of power at Niagara, so that the situation may be better understood.

There is a treaty between the United States and Great Britain in regard to the use of boundary waters between the United States and Canada, and it definitely agrees on the amounts of water that may be used on each side of the river at Niagara Falls. This treaty went into effect in May, 1910, and following is a paragraph relating to the diversion of water for power purposes:

"The United States may authorize and permit the diversion within the State of New York of the waters of the river above the Falls of Niagara for power purposes not exceeding in the aggregate a daily diversion at the rate of 20,000 cubic feet of water per second,"

and it permits

"the diversion within the Province of Ontario of the water of said river above the Falls of Niagara for power purposes not exceeding in the aggregate a daily diversion at the rate of 36,000 cubic feet of water per second."

"This shall not apply to the diversion of water for sanitary or domestic purposes or for the service of canals for the purpose of navigation."

This permits a total diversion from Niagara Falls of 56,000 cubic feet of water per second from an average flow of the Niagara River of 212,000 cubic feet per second, or a diversion of 26 percent of the average flow.

The quantities permitted in the treaty were not determined until a thorough investigation of the diversion of water had been made by government engineers as to what effect, if any, this diversion would have on the scenic grandeur of Niagara Falls and the effect on navigation in Lake Erie and the Niagara River.

Previous to the 1910 treaty the use of 15,600 cubic feet per second had been allowed by the Burton Bill for power purposes in New York, with the possibility of having this increased if for a period of six months it had all been used.

The treaty has now been in effect for six years. The power companies on the United States side of the river have for years used all the water which the government will allow, which is 4,400 cubic feet per second less than the treaty provides. Notwithstanding the great demand for more power in the United States, this 4,400 cubic feet of water per second is going to waste over the Falls.

The power companies have asked the government for permits to use it and are ready and desirous to convert it into electrical energy, but the United States government withholds the necessary permits. This 4,400 cubic feet per second is capable of developing about 80,000 h. p. If this amount of electrical power were developed by steam power, it would require a ton of coal every minute, or 525,600 tons per year. Is this worth saving? It certainly is and should be, if it can be saved without destroying the scenic grandeur of Niagara or without adversely affecting navigation.

The United States Government Engineers' investigation was under way for four years previous to the signing of the treaty and was very carefully and scientifically made and covered in a report to the 62d Congress, Senate Document 105 and H. R. Document 246. The conclusions from the Government Engineers' reports regarding the American Fall were that about five percent of the flow of the Niagara River goes over it and that there is no lessening of scenic grandeur due either to water diversion for power purposes or from natural causes. The conclu-

sions reached regarding the Horseshoe Fall were that the scenic grandeur had been impaired by depletion of water at the extreme ends of the Horseshoe, but that this is principally due to natural causes.

The impairment to the Horseshoe Fall is principally due to the recession of the rock at the apex of this fall, which diverts the water from the sides of the horseshoe. Any diversion of water for power purposes tends to still further reduce the flow over the sides of the horseshoe, but the report states that the lessening of the flow over the sides "and that which may be anticipated from further diversions and from lower stages in Lake Erie may be largely, if not entirely, remedied by a submerged dam placed in the bed of the river immediately above the Horseshoe Fall, with the object of diverting a portion of the great volume passing over the center or apex of the Horseshoe so as to increase the depleted ends of that fall, and, incidentally, diminishing the rate of recession of the apex."

Although the remedy for the thinning of the flow of water over the ends was shown to be practical about eight years ago, there has been no attempt to apply it by either of the governments interested or by anyone else.

If the scenic grandeur of the Horseshoe Fall has been lessened by either water diversion for power purposes or from natural causes, then the governments interested should without delay follow the advice of their engineers and put in the submerged dams. The question of expense would not hinder this project, as it is small in comparison to the enormous value of water for power purposes and the great value to the public as one of the greatest scenic wonders of the world. Doubtless the power companies would stand their respective shares of the expense without objection. Why, then, has not this remedy been applied? The only logical reason to those familiar with the visible features of the Falls is that the impairment of scenic grandeur has been so slight that it is not considered worth while to take any trouble or expend any money for the possible improvement. The same conclusion is reached in the same way in regard to navigation. The same Government Engineers' report previously referred to states "that the investigations have established a real, though relatively small reduction in the depth of Lake Erie, amounting

to 0.07 foot (2.1 cm.) for the present authorized diversion." This can also be compensated for by remedial dams or weirs in the Niagara River.

Maintaining the elevation of Lake Erie water level is of tremendous commercial importance to the shipping interests, and the cost of building remedial works is insignificant compared to the interests involved; but, notwithstanding this, no attempt has been made to build remedial works up to the present time.

Why should remedial works be built to compensate for the variation of the level of Lake Erie of about one inch, due to water diversion for power purposes at Niagara Falls, when the variation of the Lake Erie level by natural causes, rainfall and varying winds is about 14 feet?

Another artificial diversion of water from Niagara Falls is made by allowing the water from Lake Michigan to flow through the Chicago Drainage Canal into the Illinois River and thence through the Mississippi River to the Gulf of Mexico.

At the time of making the treaty regarding the division of water for power purposes at Niagara Falls between the United States and Canada, it was assumed that the Chicago Drainage Canal would take 10,000 cubic feet per second, and this accounts for part of the difference of the unequal division of water there by the treaty.

The principal importance of the diversion of water through the Drainage Canal is for the carrying away of Chicago's sewerage and, incidentally, some power is developed at Lockport, Illinois, at approximately 30 ft. head. The operation of the Drainage Canal with the full flow of 10,000 cubic feet per second is not allowed by the United States Government, but it is operated at about 7,000 cubic feet per second. Therefore, there is about 3,000 cubic feet per second which was contemplated being diverted from Niagara Falls when the treaty was made but is not now used. If this is properly used for power purposes at Niagara Falls it represents 60,000 H. P., or the equivalent of 390,000 tons of coal per year if this amount of power should be developed by steam.

Considering the use of water for power purposes as between Niagara Falls and Lockport, Illinois, the same quantity of water will develop about seven times as much at Niagara on account of

the greater "head" there, so no more water should be diverted through the Chicago Drainage Canal than is absolutely needed for sewerage purposes. Even using water for this purpose at this place is open to criticism. The emptying of large quantities of sewerage into streams passing through many villages, towns and cities is ever a menace to the health and comfort of the members of the communities through which they pass and can be considered only as a relic of old and antiquated methods.

There are two large power companies on the United States side of Niagara Falls and three on the Canadian side. A small amount of water is allowed for power purposes from the Erie Canal in New York State and also some is allowed for power purposes from the Welland Canal in Canada. Both of these uses divert water from Niagara Falls.

The total amount of water now being used at Niagara and on the Erie Canal in the United States is 15,600 cubic feet per second, from which about 215,000 H. P. is developed, and this is all used in the United States. The total amount of water now being used at Niagara and on the Welland Canal in Canada is about 29,000 cubic feet per second, from which about 360,000 H. P. is developed, of which about 175,000 H. P. is transmitted to the United States. The total amount of water diverted from Niagara for power purposes in both the United States and Canada, but not including the Chicago Drainage Canal, is 44,600 cubic feet per second, which represents a total power development of 575,000 H. P., 185,000 H. P. being used in Canada, and 390,000 H. P. in the United States.

The grants or permits under which the power companies on the Canadian side were built provided that half of the output of the power houses on the Canadian should be reserved for Canadian demand when wanted. Nearly one-half of the combined output from the various power houses on the Canadian side is now being transmitted to the United States and, therefore, there is little prospect of further relief for the demand for power on this side of the river from Canada. The development of additional power in Canada is needed there, and this will undoubtedly be completed up to the full amount of water limited by treaty as soon as the actual work can be done.

Aside from protecting Niagara Falls from the possibility of

too much diversion of water for power purposes, something must be done and done soon to preserve the Horseshoe Fall from itself, for it is literally "eating itself up." The recession of rock at the apex, due to the action of the large quantity of water flowing at that place, is going faster and faster. Over the period from 1875 to 1906 the recession averaged 5 feet (1.5 m.) per year, and since then about 8 feet (2.4 m.) per year, and during one of the recent years a great piece of rock fell out, making a noticeable change in appearance of the apex. The more the rock recedes, the more the water is diverted from the sides of the Horseshoe and the larger the quantity of water going into the gap made by the recession. How long will it take before the scenic grandeur is destroyed? Nobody can say, but this is certain, that the Horseshoe Fall is changing and the changes in the future will be much more rapid than the changes in the past, and, if we do not wish to take a chance that the changed fall will soon be much less of a great world spectacle than now, the recommendation of the Government Engineers should be followed and submerged dams built to distribute the water to give the best scenic effect and to prevent further serious recession of the apex.

An eminent engineer, resident at Niagara Falls, who has made a careful study of the hydraulic and scenic conditions lasting over a period of many years, is of the opinion that by the placing of submerged weirs just above the apex of the horseshoe and at the upper end of the rapids above the Falls, double the amount of water allowed by the treaty, or about 50 percent of the total average flow of the Niagara River, could be diverted from the Falls without serious detriment to their scenic grandeur.

If this opinion is correct, think of what economic importance it is to the people and industries within commercial transmission distance of Niagara and, more or less indirectly, for many industries scattered over the United States and Canada.

An additional 25 percent of the average flow of the Niagara River, if properly converted into power, would equal about 1,000,000 H. P., or the equivalent of 6,500,000 tons of coal each year if produced by steam power.

It is a crime to ourselves to waste such an opportunity for the development of industries, transportation and domestic conveni-

ences, and a crime against future generations not to conserve our natural resources.

After carefully considering the interests of the public in the scenic grandeur of the Falls, the benefits to them of cheap and ample power, the interests of navigation in the upper Niagara River and Lake Erie, the interests of the industries whose existence depends on low-priced power in large quantities, and the interests of the power companies, it appears that the United States Government, through the Secretary of War, who now has the authority, should without delay grant to the United States power companies the right to use the 4,400 cubic feet of water per second still allowable under the treaty, and then the two governments should jointly proceed with the recommendations of the engineers by the building of the submerged dams and remedial works, thus protecting the Horseshoe Fall from self-destruction, maintaining the scenic grandeur of both falls, improving navigation in the upper Niagara River and Lake Erie, and making it possible to still further divert water for power purposes, thereby conferring a great benefit on the population within electrical transmission distance and conserving our natural resources.

How will these questions of such great importance be decided?

There are many independent interests involved and these must be brought together and unite on the best course to pursue.

This Society might invite representatives of all the parties interested to form a commission, to investigate all features in connection with preserving the scenic grandeur of Niagara Falls, the diverting of additional water for power purposes and the improving of navigation.

It is suggested that representatives be invited, one each from the Dominion of Canada Engineers and the United States Government Engineers, one each from Canada and the United States representing the public interest in the scenic grandeur of the Falls, one representative for the Canadian power companies and one for the United States power companies, one each for the Canadian and United States industries using Niagara power and one each from Canada and the United States representing navigation interests. This commission should be empowered by the interests they represent to energetically spend as much time and

money as is necessary to obtain the information and engineering data and, within reasonable time, formulate recommendations and submit them to the Secretary of State of the United States and the Governor General of the Dominion of Canada for action.

II. ELECTRIC FURNACE PRODUCTS.

By F. J. Tone.

The development of Niagara power in 1895, only twenty years ago, marks the beginning of the electric furnace art. It stands today as one of the big factors in our industrial life. Up to 1895, when Charles M. Hall came to Niagara, the aluminum industry depending on steam power had given little promise of commercial success. Its almost incredible development during twenty years has been due to the impetus of Niagara power, and its future magnitude no one dares to predict. Dr. E. G. Acheson with a 150-horsepower furnace operated by electric power generated from steam had made a commercial failure of carborundum. Coming to Niagara in 1895 he was at once enabled to found the artificial abrasive industry. Willson, the inventor of calcium carbide, was working at Spray, North Carolina, with a 200-horsepower furnace. Today we have 12,000 to 15,000 horsepower furnaces making almost as much carbide in one day as the former furnace produced in a year.

With the technology of these great industries, aluminum, calcium carbide, cyanamid, abrasives, ferro-alloys, silicon and graphite we are all familiar, but few realize their economic importance or to what an extent the industrial and metallurgical arts are indebted to Niagara power for their development. At this time, when we are taking stock of our industrial assets and determining how the nation can best make itself industrially self-contained, it is well to point out how the products of Niagara power are bound up with this whole broad question.

FERRO-SILICON.

The manufacture of steel is the greatest of all American industries, and its dependence on Niagara power is strikingly illustrated

by a study of the ferro-alloy industry. In 1915 the estimated production of finished steel in the United States was 28,000,000 tons, and in a major portion of this there was employed as the chief deoxidizing agent high-grade electrically-produced ferro-silicon. This alloy is used in practically all steel manufactured by the basic open-hearth process, which in recent years has so far supplanted the Bessemer process as to account for more than 70 percent of the total production. To a lesser extent electrically-produced ferro-silicon is used in almost all the other processes of steel manufacturing.

The steel-casting industry finds high-grade ferro-silicon practically indispensable for eliminating blow-holes and producing sound castings. The extension in the use of cast steel as a material of engineering during the past twenty years is due primarily to an adequate supply of high-grade ferro-silicon, insuring complete deoxidation of the molten steel. The cast-iron foundry industry has in recent years realized the advantages of the use of high-grade ferro-silicon, and progressive establishments now depend on this alloy for a control of their castings.

Niagara Falls is the home of ferro-silicon in the United States, and up to the present time the total domestic production has been made from Niagara power. For a short time prior to the European War some ferro-silicon was imported, but a large portion of this was produced by Niagara Falls power in Canada. The Canadian producer has, since the war began, been compelled by government order to export ferro-silicon to countries other than the United States, thus increasing an existing unprecedented demand for the domestic product and causing a power famine on the American side of the Niagara River. This fact has a significant bearing, not only on the inadequacy of the total supply of Niagara Falls power, but on the regulations which govern the importation of electrical energy into the United States. A cessation of the supply of ferro-silicon would be nothing short of a calamity to the steel business, and when we further consider that specifications for shell steel for munition purposes call for 0.20 to 0.30 percent silicon, we see the *rôle* ferro-silicon plays in munition manufacture and the realization of our own program of preparedness.

FERRO-CHROMIUM.

The essential element in the manufacture of successful armor-plate and armor-piercing projectiles is introduced into steel by the alloy ferro-chromium. It is strictly an electric furnace product. Without this alloy not a battleship could be provided with protective armor nor a coast defense gun served with modern projectiles. More than one-half of that now consumed in the United States is produced at Niagara Falls. Ferro-chromium likewise enters into the manufacture of automobile steels, steels for jaws, balls, linings of crushing machinery, dies and a variety of special steels.

Sir Robert Hadfield has compared the striking energy of an armor-piercing projectile with that of a modern express train. He states that a 14-inch (35 cm.) projectile weighing 0.62 ton and fired so as to pierce 12-inch (30 cm.) armor plate at a distance of eight miles (13 km.) must have a striking energy of 30,000 foot tons (9,000 m. tons) and a striking velocity of 1,700 feet (510 m.) per second, or twice the energy of a modern express train running at forty miles (67 km.) per hour. The shell has 1/8000 the bulk of the train, and the metallurgist has been able to provide a shell having a steel point of such quality that it delivers this concentrated energy upon the hard-faced plate and passes through it without suffering deformation. This is a striking metallurgical achievement, but it is the electric furnace and ferro-chromium that have made it possible.

TUNGSTEN-VANADIUM-MOLYBDENUM.

These alloys are made in part from Niagara power, and when made elsewhere there is largely used as a reducing agent metallic aluminum, also a Niagara product. They form the chief constituents of a relatively high-priced group of products representing an annual production of several millions of dollars, and which in conjunction with chromium are absolutely necessary in the manufacture of high-speed tool-steel, magnet-steel, certain gun-steels, and a variety of special steels. High-speed steel furnishes a most striking example of the dependence of the metal-cutting industries on products of Niagara power. To one familiar with machine-shop practice under the limitations of carbon steel, where

it was necessary to maintain a cool cutting edge, it is amazing to see a 17-inch (43 cm.) forged shaft destined for some battleship revolving at a surface speed of 30 feet (9 m.) per minute, the tool of high-speed steel working at red heat, and chips 1½ inches (4 cm.) wide and ⅝ inch (1.4 cm.) thick coming off, colored a deep blue. Ferro-chrome and the other alloys of this group have made this possible. High-speed steel has tripled the capacity of every machine shop in the world and the efficiency of every workman. It has cut to one-third the capital invested in tools to accomplish a given volume of work.

Considering the metals or alloys of chromium, tungsten, vanadium and molybdenum as a group, it may be positively stated that in the absence of these products we should not be in a position to build modern battleships, guns, submarines and many other machines necessary for the nation's defense, to proceed with thousands of operations involving the cutting of metals at a rate comparable with the present or necessary to successfully meet foreign competition. A goodly proportion of our steel and metal working industries, mining operations and scores of other industries would find themselves in the condition of practically twenty years ago.

FERRO-TITANIUM.

Titanium as a ferro-carbon-titanium alloy is employed in a large tonnage of steel made by the Bessemer and open-hearth processes, as well as in the production of steel and iron castings. The aluminum bronze and other non-ferrous alloy industries are being greatly benefited by the use of titanium alloys. It is worthy of note that the smelting of titanium alloys by other than an electric furnace process is commercially impracticable.

SILICON-METAL.

A special steel of great importance to electrical industry is silicon steel, used in electrical transformer construction and all alternating-current apparatus. Silicon metal and 75 percent ferro-silicon essential in its manufacture are produced only at Niagara Falls. The ageing of transformer steel has long been the cause of a serious falling off in efficiency. This loss often doubled after a few years' use. Silicon steel does not age. Moreover, its original

hysteresis loss is 25 percent less than that of the old type of steel. The saving in a large generating and distributing system from the generator through step-up and step-down transformers to the motor may be as high as 6 percent. Thus silicon steel, a comparatively unknown product, is saving many millions of dollars annually wherever electric energy is transformed.

Silicon metal as a "preparedness" product is important in the generation of hydrogen for aeronautical purposes. In conjunction with caustic soda it forms the cheapest method of generating hydrogen in the field or on shipboard when portable outfits are required.

ALUMINUM.

The manufacture of aluminum is the largest of the electrochemical industries in point of power consumed and value of product. Commercial development was made possible by Niagara power, and Niagara Falls was for many years the only seat of the industry. The chief uses of aluminum are in automobile and aeroplane parts, electric transmission lines, cooking utensils, acid containers, the deoxidizing of steel and alumino-thermic welding. Even with the prodigious increase in production the scarcity of aluminum is today very acute and is regarded by automobile engineers as little less than a calamity.

ABRASIVES.

The electric furnace abrasives, carborundum and alundum, are fundamental elements in the metal-working industries. They have revolutionized the methods of finishing metal parts, just as high-speed steel has revolutionized the art of shaping metals by cutting. Artificial abrasives have been gradually displacing natural emery and corundum, until in 1914 they constituted 62 percent of the total abrasives used in the United States. The natural abrasives have practically all been imported, and comprise Turkish and Grecian emery. With the beginning of the war, mining in Greece and Turkey ceased and artificial abrasives have been called on to supply the whole field. There are five plants making artificial abrasives from Niagara power, three of which are on the American and two on the Canadian side of the river.

The great metal working industries making agricultural imple-

ments, locomotives, cash registers, electrical machinery, fire-arms, flour-milling machinery, paper machines, automobiles and all castings of steel, iron and brass are entirely dependent today for an adequate supply of grinding materials on Niagara power. As a simple example, take the automobile industry. The mechanical perfection of the modern automobile and the interchangeability of parts have been made possible only by the development of the grinding machine and the grinding wheel. Practically all parts of an automobile are finished with abrasives at some stage of their manufacture. Crankshafts are roughened and finished with grinding wheels, likewise camshafts, pistons, cylinders, and all forgings and castings. It is impossible to produce ball-bearings and roller bearings without the use of grinding wheels. Cut off the artificial abrasives and force the automobile manufacturer to go back to the grindstone, at the same time eliminating the other products of Niagara power, aluminum, high-speed steel and special steels, and we would see a works which now produces 500 cars per day reduced to an output of considerably less than 100 cars, with the same force of workmen and the same plant equipment. This would mean such an increase in price that there would be no automobile industry on its present existing lines.

Manganese steel, one of the unique materials of engineering, was little known fifteen years ago. Today the output in frogs and switches, burglar-proof safes, dredges, gears and rolls represents many millions of dollars. No steel tool will cut it. Without grinding wheels to shape and fashion manganese steel, it would still be a metallurgical curiosity.

CALCIUM CARBIDE.

This electric furnace product is the only commercial source of acetylene. Its principal uses are in the lighting of small towns, isolated hotels, institutions and factories, in the lighting of railway trains and harbor buoys, in the form of portable lamps for miners and automobiles, and in a more recent and exceedingly important application of this gas to the oxy-acetylene cutting and welding of metals. A cessation in the domestic production of calcium carbide would entail enormous loss. Had we to do without acetylene lighting and the recent application of the oxy-acetylene flame in the welding of metals, in the building as well as

the razing of large metal structures and as a means of effecting economies in a great variety of other ways, we should as a nation be compelled to work at a slower and less efficient rate than our competitors in many of the metal industries.

Calcium carbide is the material from which is produced calcium cyanamid, the most important compound today in the field of fixation of atmospheric nitrogen, and the source of supply which could be most promptly and positively relied upon to solve the problem of an adequate supply of nitric acid and nitrates employed in munitions of war in the event of a failure of the supply of Chilean nitrate. To manufacture these products to the extent required for self-preservation would necessitate a much larger diversion of water of the Niagara River than is at present permitted.

ARTIFICIAL GRAPHITE.

This is an electric furnace industry that owes its inception and entire development to Niagara power. The production, which totals several thousand tons annually, falls in two general classes, electrodes and powdered graphite.

Graphite electrodes are used exclusively as anodes in all electrolytic cells for the production of caustic and chlorine. They are a fundamental requisite of this vast industry. With the supply of platinum cut off they are now replacing this expensive metal as anodes in the electrolytic chlorate processes. Graphite electrodes are extensively used in electric smelting and refining furnaces, producing high-grade steel, alloy-steels, ferro-alloys, copper, zinc and nickel.

The chief uses of powdered graphite are in dry cells, paints and lubricants. Every one of the millions of flash-light batteries produced in this country contains artificial graphite.

All the manufactured graphite used in the world is produced at Niagara Falls. It occupies a field of its own, which cannot be filled by natural graphite, and it is another striking illustration of the electric furnace "going nature one better."

Thus we see that the electric furnace is not merely a new metallurgical tool but an important element in our economic life. Dr. E. F. Roeber, in a remarkable address before this Society, once pointed out that we need a revaluation of our aesthetic values.

There is beauty in electrochemistry. There is beauty in ferro-chromium, when high-speed steel cuts human toil in half. There is beauty in fixed nitrogen, when it feeds a teeming population. When future generations begin to shiver for want of coal and to starve for want of nitrogen, the present generation will be remembered not as champions of the preservation of scenic beauty but as champions of the ugliness of wasted resources.

III. THE CHEMICAL INDUSTRIES.

By A. H. Hooker.

It is interesting to note how a despised and perhaps, for the time, a harmful by-product, may develop into the chief product of an industry, and a shortage seriously affect the general comfort and economy of our lives.

Just now gasolene is an everyday example. In the time of the early coal-oil lamp, many dangers lurked in the poorly refined oil, and every effort was made to increase the yield of high-flash kerosene and remove for this reason gasolene from the oil. This gasolene was then little more than a waste product, to be disposed of when possible or thrown away and allowed to evaporate, or even run into the rivers with the resulting danger of fire. Now all is changed, and the utmost effort of the chemist and engineer is called for to devise means of increasing the yield of this despised by-product at the expense of the higher boiling fractions in the crude oil. The Government takes part in the research to meet the situation, and even legislation is asked for to assist in regulating the supply and demand.

Chlorine produced in this country entirely by electrolytic processes and with Niagara Falls as the center of the industry, offers another example of an originally annoying by-product becoming a necessity.

It is no flight of fancy to say that our lives and the lives of our families in Niagara Falls, Buffalo and over one thousand other cities, depend on the use of either liquid chlorine or chlorine in the form of "bleaching powder" or hypochlorite for the sterilization of our water supplies to a point where epidemics of typhoid

are avoided. Niagara Falls, now free from typhoid, was a plague spot, nothing less, until we improved our filter system and treated the water with hypochlorite or chlorine. Our own army is now using the same chlorine treatment to avoid the dangers from typhoid, which beset our soldiers during the Spanish-American war. In Europe the best preventative of blood poisoning and infection from dirty wounds is reported to be a mixture prepared from "chloride of lime" or "bleaching powder." Without this same "bleaching powder," our mills and printing establishments turning out or using book paper and writing paper could not turn out their product; our cotton dresses and sheeting would no longer be white; our shirts and collars from the laundry would be a dirty yellow; and, what is worse, a serious menace to health would result through lack of disinfection. Also, white cotton batting, bleached shellac, chloroform for surgical operations, even the disinfection of our garbage and sinks, call for chlorine in the form of "Bleach." This same chlorine is used for the production of carbon tetrachloride, which in the form of "Pyrene" has become a household necessity as a fire extinguisher.

To meet the shortage in coal-tar dyes, by the combination of chlorine with coal-tar benzol and toluol, we are now beginning to produce in quantity those necessary "intermediates" formerly made in Germany, from which are made sulphur black, picric acid, benzoic acid, trinitrotoluol, benzaldehyde or "oil of bitter almonds," and dozens of other products of like nature for which we are beginning to feel such urgent need.

Side by side with the production of electrolytic chlorine, we have caustic soda and caustic potash, resulting from the same electrolysis of either sodium chloride or potassium chloride. Caustic soda and caustic potash are equally indispensable in our daily economy. The amount of soap used per capita is said to mark the state of civilization of a people. Without these alkalies we cannot make soap, and it is equally important for the production of mercerized cotton, refining of oils, the manufacture of dyes, explosives, pigments, and many chemicals and medicines, the cleaning of metals for electroplating, and in the small can of household lye with its dozens of uses.

At several of the plants at Niagara Falls, the electrolysis of chloride solutions takes place in cells where the products are

directly united to form chlorate of potash or chlorate of soda. Every match we strike, every primer for a rifle cartridge, contains chlorate. Also, it is a necessity for certain dyes and colors, and we may even use it in our tooth wash or as a lozenge for a sore throat.

A reference to the by-product stage of chlorine is perhaps of interest. The great heavy chemical industry of England developed from the acid and soda plants using the Leblanc process for the manufacture of alkali. The principal product sought for was soda ash obtained by decomposing salt, and the chlorine, driven off in the form of hydrochloric acid, was produced, as the industry grew, far in excess of any demand. As a by-product, this was allowed to escape from the chimney top, to the detriment of surrounding vegetation, or it was run into the rivers where it destroyed the fish until the authorities called for some means of abating this nuisance. It was then that the hydrochloric acid was treated with manganese, and the free chlorine in turn absorbed by lime to form "bleach." As this chlorine was considered a valueless by-product, all that was considered necessary was to create a market which would perhaps pay for the lime, package and handling, and the early price for this by-product "bleach" was therefore very low. Gradually, however, a demand for the product was created, and a new industry, the bleaching of cotton and wood pulp, came into existence.

At this time, the Solvay process for the manufacture of soda ash was developed; a process which was able to produce soda ash and leave the chlorine in a harmless form as calcium chloride, and at the same time produce this soda ash at a much lower price than had been charged by the old Leblanc process. The old process had found a very satisfactory profit selling soda ash at $60.00 per ton, and "chloride of lime" at perhaps $12.00 per ton. When the Solvay people began to offer soda ash at $30.00 to $40.00 a ton, the Leblanc plants were unable to compete, and one after the other began to close down. To whatever extent this closing down took place, there developed a shortage of "bleaching powder" and muriatic acid, and in a very short time the price of bleaching powder was increased, owing to this demand and shortage, from $12.00 a ton up to $40.00 or $50.00 a ton. The result was that the Leblanc plants were able to compete with the Solvay plants

and reduce their price of soda ash accordingly, so long as they were able to obtain the higher prices for "bleaching powder" which now, of course, became their principal product and not a by-product, and caustic soda a secondary product. Again the pendulum has swung and we have chlorine as the principal but limiting factor around which the electrolytic production of caustic and chlorine products is built.

Turning again to the electrolytic products of soda at Niagara, we find the production of metallic sodium taking an important place. This forms the basis for the manufacture of the sodium cyanide supply of the country, and without this many of our most important gold and silver mines would be compelled to shut down, to say nothing of the great plants dependent upon the use of cyanide in electroplating. This same sodium is the basis again for sodium peroxide, used by the analyst as a means of determining fuel values, and as a means of generating oxygen for laboratory use, or in hospitals and in submarines and mine rescue apparatus for preserving the breath of life. It is also used for the manufacture of hydrogen peroxide, used not only for bleaching purposes but also entering so freely into our daily lives as a simple household disinfectant.

Another electrochemical industry which has its chief center in Niagara Falls is the production of phosphorus. While yellow phosphorus is no longer used in the manufacture of matches, the sesqui-sulphide is an essential ingredient in the "strike-anywhere" match, and amorphous phosphorus in the safety match. Whenever you strike a match (not made in Sweden) think of chlorates and phosphorus made by Niagara power, and contemplate the possibility of a general return to the use of the flint and steel of our grandfathers' time, should these industries be expatriated (to Norway for example) for cheap power, and an embargo like the present one exist. Phosphorus also finds an important and irreplaceable use in the metal industry as a deoxidizer and hardener in certain non-ferrous alloys, chiefly in the phosphorizing of copper for the manufacture of phosphor bronze used on battleships and for certain bearings on machines, automobiles and some chemical apparatus.

To sum up it will be seen that a large number of our most important manufactures and products of the utmost importance

to the country are directly dependent upon the electrochemical industry at Niagara Falls. Among these we find the paper mills, soap factories, gold mines, the manufacture of chloroform, disinfectants, matches, explosives and dyes, water purification, cotton finishing, oil purification, and a dozen other activities which would be seriously hampered or closed entirely without the chemicals electrolytically produced at Niagara.

Permanent chemical self-containedness and preparedness to keep pace with this country's growing needs and population calls of necessity for an increase in the production of these plants. This increase cannot take place without an increased power consumption. The needed power stands ready for development without injuring in the slightest degree the scenic beauty of the Falls. The skill, energy and ability to utilize this power for the needs of the country are at hand. Only a maudlin sentimentality, not based on fact, stands in the way of a greater development and infinite gain to the country.

We have already noted the fact that some of the coal-tar "intermediates" so much needed for the manufacture of dyes, explosives and medicinal preparations, are now being made at Niagara Falls. As a rule these products need nitrogen to complete the product—nitric acid or ammonia—and this can be obtained by the fixation of atmospheric nitrogen by means of cheap electric power. The same fixed nitrogen is of equal importance to the agricultural interests of the country. The art is well started, but still in its infancy, and tremendous advantages to the entire country must ultimately accrue from the solution of the cheap fixation of nitrogen.

Let me close by repeating what I said in New York in February at a local section meeting:

"As this was written, I saw from my window the waters of the Niagara River flowing by with a capability of being developed into perhaps five million horsepower—the most uniform and constant water power in the world. I am very fond of the impressive beauty of its mighty Falls and the wonderful gorge and rapids below, and only as a last resort in the event of a national defense necessity would I do anything to injure that landscape. Such injury, however, is not necessary. As I study the daily moods of the Falls, I see the ebb and flow of water due to the direction

and velocity of the wind on Lake Erie, making far greater differences in the volume of water passing over the brink of the Falls than is caused by the present diversion of water producing some five hundred thousand horsepower. I also see that the beauty of the Falls is not at its best when the largest volume of water is passing over its brink. From careful study I am satisfied that well over one million horsepower more could be diverted, and not an iota of injury would be done to the scenic grandeur of the Cataract if a little engineering skill were used in placing the proper breaks and deflectors. If this is true, think of the tremendous increase in national efficiency and preparedness this development would mean! Arrange now with Canada for a development of water power at Niagara three times as great as at present—the time is ripe.

"For every one hundred thousand horsepower diverted, provide say ten thousand horsepower shall be devoted to the fixation of atmospheric nitrogen. The more varied the methods used the better. *Make Niagara the commercial research laboratory of the nation* in this field by supplying private enterprise with power at nominal cost for this purpose. Under these conditions, power, even if developed by private enterprise in large amounts, could in the above percentage be supplied as cheaply if need be as Norwegian power, and would be infinitely better adapted and centralizd for the purpose. Such power would be within a night's ride of Washington, New York or Chicago. Already located at Niagara Falls is the largest group of electrochemical workers in the world. Such a development would double their number.

"Is it through lack of foresight, or 'a dog in the manger policy' that some of our largest and most important electrochemical industries are even now compelled through lack of cheap power to go to Norway and other fields, there to start the training of a foreign army of electrochemical workers upon foreign soil, while unused water which could be utilized without injury goes to waste?

"I have been told that the Niagara River is a border stream; that plants situated near that border would be peculiarly open to foreign attack. Conceding that England be our enemy this is true. But did Germany give heed to an even stronger reason against making her experimental and peaceful development in

Norway, where, as at Niagara, the economic conditions were right?

"Not in a day, a month, nor a year can these problems, alike of peace and war, be worked out, the equipment developed and installed, and above all the workers trained. The goal is an ever-increasing internal independence both as regards food and chemicals. For an increasing population, this may well mean the regeneration of a worn-out soil, the re-fertilization of our farm lands from New England to the West with ammonia and nitrates from the air."

IV. THE NITROGEN INDUSTRY.

By W. S. Landis.

The commercial fixation of atmospheric nitrogen has developed along three distinct and independent lines—the absorption by carbides, as exemplified in the present Cyanamid Process; the direct oxidation to oxides of nitrogen with subsequent formation of nitric acid, as represented by the Arc Processes; and the direct combination with hydrogen to form ammonia, as developed in the Haber Process. Chronologically these three processes were developed in the order given above.

The original work of Frank and Caro, antedating the cyanamid process, started about 1895. The organization controlling the present industry was not formed until 1904, in which year we might really date the first beginnings of the commercial applicataion. In 1906 the first factory was completed and began manufacturing on a considerable scale, but progress was slow until 1910 when the industry received a new impetus and production began simultaneously in various parts of the world. It was in this year, 1910, that steady production began at Niagara Falls, Canada, that plant having been completed late in 1909.

We are all familiar with the work done by Bradley and Lovejoy at Niagara in 1902, and while this initial installation did not prove the foundation of a commercial development, it directed attention to the arc process, and may be said to mark the beginnings of this great branch of the industry. In this same year, 1902, Birkeland

and Eyde began taking out their patents, followed by the development of the great Norwegian plants. The following brief tabulation shows the growth of this industry in its early period:

Year.	H. P. Used.
1903	3
	150
1904	1,000
1905	2,500
1907	40,000
1911	55,000

In 1905 the Badische Company erected a small experimental factory in Norway for the development of Dr. Schönherr's arc furnace, which factory was enlarged in 1907. In that year it was using about 1,400 kilowatts. Later the Schönherr and Eyde processes were taken over by a new company, and the two furnaces have been operated side by side in the same factory. New installations at present going into operation will not employ the Schönherr furnace, so that the Norwegian developments will probably in the future all be directed to the use of the Birkeland-Eyde furnaces and process.

In 1906 the Paulings began experimenting with a new type of arc furnace for the oxidation of nitrogen, and in 1909 a commercial plant was erected at Innsbruck. This initial factory used approximately 15,000 H. P. and was followed a year or so later by a 10,000 H. P. plant in Italy, and a 25,000 H. P. plant in France.

The Pauling process, however, has never attained very marked development for various reasons, and a small plant erected some years ago in this country has passed through a somewhat precarious existence, and will probably sooner or later be abandoned because existing conditions are not favorable to its commercial development.

The third and last of our processes for the synthetic production of ammonia has been in the hands of the scientist for many years. About 1905 the first promise of success appeared in the publications of Professor Haber, though no actual commercial progress was made in the matter until 1909 and 1910, when patents began to appear covering suitable catalytic agents. This process came under the control of the Badische Company, who spent several

years of active development on it, and it was not until 1913 that commercial production was assumed. In 1913 and 1914 synthetic ammonia was produced on a fair scale by the Badische Company, but the process itself has not found a place outside of Germany, though attempts were made to introduce it into this country as late as 1914.

Recent developments in the nitrogen fixation industry have been on a scale unheard of in the world's history. Installed capacity for nitrogen fixation, expressed in short tons nitrogen per year, in 1913 and at the beginning of 1916, throughout the world are shown below:

	Short Tons Nitrogen Per Year.	
	1913	1916
Cyanamid	65,590	209,510
Arc Processes	18,650	29,400
Synthetic Ammonia Processes	8,000	60,000
Total	92,240	298,910

As most of this increase was made in 1915 we note that in practically one year the industry showed an *increase* of more than 200 percent. One million horsepower is now consumed in the three groups of processes enumerated above.

The arc process up to the outbreak of the war did not find a secure place outside of Norway. Germany has erected only one new small plant (15,000 H. P.). The Haber process still rests in the hands of the original developers in Germany, and no successful attempts have been made to transplant it from its place of origin. The cyanamid process has now large plants scattered throughout the world in Norway, Sweden, France, Italy, Germany, Austria, Switzerland, Japan and Canada.

Turning to another phase of the subject we find that these nitrogen fixation processes all require electric power for their operation. The arc process produces nitric acid directly, and uses nearly 3 H. P. years of electrical energy per ton of HNO_3 produced, with small quantities of miscellaneous raw materials entering largely into recoveries of waste and the production of by-products.

The Haber process, whose sole product is ammonia, uses considerable quantities of energy, though little is heard of this phase

of the process—fully one-sixth the requirements of a well conducted cyanamid plant. In addition it uses much fuel, and a large amount of highly skilled labor, so that careful investigations have proven that this process will with difficulty find satisfactory competitive fields outside of its country of origin.

The cyanamid process primarily produces cyanamid, a material which finds application directly as a fertilizer, or as a raw material for the production of many organic derivatives. It is a simple matter to transform the nitrogen in the cyanamid into ammonia, which finds further uses as ammonia liquor, anhydrous ammonia, a chemical reagent in itself, or as a commercial fertilizer directly in the form of either ammonium phosphate or ammonium sulphate. Further, it is commercially possible to oxidize this pure ammonia into nitric acid at high efficiency, and with the consumption of a negligible amount of electric power. Assuming, for the sake of comparison, that the end product of the cyanamid process is nitric acid, the power consumption required for fixing a unit of nitrogen by this process is only one-fifth to one-sixth that of the arc process. It is true that the cyanamid process uses raw materials in the form of lime and coke, but in this country these are extremely cheap and plentiful, and their cost is many times counter-balanced by the extremely great saving in power incident to the use of this process. Outside of a few skilled mechanics and electricians all the labor required may be of the most ordinary grade, and no trouble has been experienced along this line in the transplanting of this industry to the many countries represented. Nitrogen products, whether in the form of nitrates or ammoniates, can be more cheaply produced by the cyanamid process than they are otherwise securable, and this, so far as Germany is concerned, has not only been appreciated, but has been acted upon until she has by the development of the fixation of atmospheric nitrogen, chiefly the cyanamid process, made herself completely independent of all outside sources of nitrogenous materials.

None of the three main nitrogenous fixation processes have found a place within the borders of the United States. On account of the excessive power requirements of the arc processes the author is of the opinion that no serious thought has existed as to its adaptability to conditions in the United States, for cheap water power in sufficient quantity is not available in such districts

as would enable the nitric acid made to compete with present sources, and as an emergency measure for munitions manufacture there is not sufficient power available to operate a plant of the necessary size.

It has been estimated by our military boards, that in the event of war, this country would need 180,000 tons of concentrated nitric acid per year. The arc processes in their present state of development could furnish this requirement with the expenditure of approximately 540,000 horsepower—20 percent more than is developed on both sides of the boundary line at Niagara Falls, the largest of our water powers. The cyanamid process could meet this emergency requirement with only 100,000 H. P.

One attempt was made to introduce the Haber process into the United States, but abandoned after mature consideration, because of the impracticability of this process competing with others as a source of ammonia in this country.

Active attempts were made several years ago to bring the cyanamid industry into the Southern States, but the policy of the Government with respect to water power absolutely prevented development at that time. Since then the serious handicap of the higher power costs in the United States has discouraged further efforts to establish this industry in the United States. Successive additions which should have been erected in the States were built to the Canadian factory where cheaper power was available.

Water power in the United States is expensive, not only because of the physical conditions which surround available water power sites, but also from the fact that hydro-electric power at practicable sites for its generation, even though it may be cheaply developed, has when developed an actual or potential value considerably in excess of what the nitrogen industry can afford to pay. Furthermore, there is a tendency for the law makers and others to view the value of water power to a community as measured solely by the price which can be secured for it from the individual customer using it for electric lights, small motors, street cars and other municipal purposes. Now a great water power converted to municipal use for the most part is of little, if any, economic importance. The difference in the cost of a kilowatt-hour of energy on the switchboard generated by steam, as compared with a kilowatt-hour of energy developed by water,

is part of a cent. Under the usual conditions of a water-power site being remote from the communities in which the power is used, the difference in cost between the power generated in the community by steam, and the power generated by water and transmitted to the community, is a bare fraction of a cent. The price of power delivered to the consumer under these conditions averages, generally speaking, 6 cents per kilowatt hour, namely, from 2 cents for large users up to 12 cents for the small users. Estimates of the saving in the use of water power as compared with steam show by specific examples that even if the customers benefited to the extent of the entire saving, the advantage to the customer would not amount to more than four to five percent of his monthly bill.

We have just reviewed the history of the nitrogen industry, and noted that it has found no place in the United States. We have further seen that cheap water power is a necessity of the industry, and that our policy of water power development has not produced, nor is it tending to, such cheapening of electrical energy as is needed to make a place for this industry. The cost of this policy, as pertaining only to this one industry, to the people of the United States may be gained from the following figures:

The import invoice values (port values less freight) of nitrate of soda and sulphate of ammonia brought into this country between the years 1910 and 1914, a period during which there have existed successful, commercial, operating nitrogen fixation plants elsewhere, amounted to $108,323,568, or an average of approximately $22,000,000 per year, all of which has actually been paid out to foreign producers of these materials—money which has actually left the country.

This tonnage was probably brought to the United States in foreign vessels, thereby adding the freight charge, or nearly $4,000,000 per annum to the above, and making a total of $25,000,000 per annum paid to our foreign business friends, who are not hampered by such difficulties as have existed in the United States. 150,000 continuous horsepower would fix this amount of nitrogen and under favorable power rates at a materially lower cost than the import invoice values quoted above.

Within the last few months this nation has been aroused to at least some little sense of the necessity for preparedness for national

defense in case of war, and there is thus brought into the nitrogen problem quite a new element, particularly so far as the necessity for immediate development is concerned. The most important new thing in the method of conducting a war is the very greatly increased consumption of explosives. Save in the fixation of atmospheric nitrogen there is only one source from which nitric acid can be secured, namely, from Chilean saltpeter, and nitric acid is the universal pre-requisite to the manufacture of military explosives.

For this purpose alone it is estimated that Germany is consuming today at the rate of practically 1,000 tons per day. Germany found from her experience in the present war what the United States should anticipate would be its fate, namely, that in any war with a stronger maritime nation the supply of Chilean nitrate would be cut off. These are the considerations in part which point to the absolute necessity for the establishment within the borders of the United States of the air nitrogen industry. The difficulty, however, is to make the undertaking securely profitable in times of peace, chiefly because the cost of power within the States is excessive as compared with the cost of it in other countries, and power in all of the commercially practicable processes is the chief item of expense in manufacture.

Is it not a logical conclusion from the above facts that the great economic use of water power is in applying it to those industries which produce a material entering into the fundamental necessities of the people, either directly or as raw materials for a succession of other refinements? One of the striking characteristics of water power is that it frequently furnishes the one and only necessary means by which new and valuable industries can be introduced and made commercially practicable. Thereby water power is properly to be credited with giving birth to the industry, and the importance of the water power under these conditions is to be measured by the fact that this industry in its turn gives new employment, not otherwise to have been had, to hundreds, and perhaps thousands, of workmen; the product in turn in its other refinements and applications gives employment to hundreds, and perhaps thousands of additional hands; and so on indefinitely. If the product is one which makes for the amelioration of the most pressing of all the modern-day evils, namely, the continually

increasing cost of living, the use of the water power in this production is the very highest economic use to which it can be put. This is precisely what water power applied to the fixation of atmospheric nitrogen does for the world, for the chief use of the product is in an agricultural fertilizer. The secret of cheaper food can only come through increased crop yield per acre cultivated without the employment of additional farm labor, and the only means to this end is a cheap and plentiful supply of artificial fertilizers.

The importance of labor-saving devices is so well recognized, and so universally accepted in the equipment of factories and mines, that it is all the more unusual that the people of the United States and the Government have not realized that in the field where the disproportion of wages between the European worker and the American worker is greater than anywhere else, adoption of the greatest of all labor-saving devices, namely, agricultural fertilizers, has not only failed to become universal, but has not been carried out at all except on the most meager scale.

DISCUSSION.

C. G. Atwater: In his paper on the nitrogen industry, Mr. Landis has ably discussed the progress made in the commercial fixation of atmospheric nitrogen in this country. No one will dispute that the development of our water powers, together with the development of these processes of recovering atmospheric nitrogen, is desirable if it can be done on a commercial basis.

There seems no reason to doubt that Mr. Landis is correct in his claim for greater efficiency of nitrogen fixation by the cyanamid process over the direct arc process. He says that to produce 180,000 tons of nitric acid by the arc process would require the development of 450,000 H. P., and to produce this by the cyanamid process would take only 100,000 H. P. But if the necessary ammonia were obtained from the by-product coke ovens, no water-power development at all would be necessary. The end product of the cyanamid process is ammonia, which places it on the same basis as the by-product coke oven or coal-

gas retort. In either case the ammonia must be oxidized to form nitric acid. Therefore it seems to me that exception may well be taken to Mr. Landis' statement that "save in the fixation of atmospheric nitrogen there is only one source from which nitric acid can be secured, namely from Chilean saltpeter."

In 1915 the United States produced about 220,000 tons of sulphate of ammonia from the coke and gas industries. Roughly speaking, this is equivalent to the same amount of nitric acid, and is already more than the 180,000 tons, according to the paper, our military boards consider would be needed per year in case of war. But aside from this, it does not appear to be generally known that there is a great increase coming in our ammonia production from the coke-oven source, which will probably increase 30,000 or 40,000 tons of ammonia sulphate in the year 1916, due to more continuous operation of the coke-oven plants already erected, and in addition there are over 2,600 new by-product coke ovens already contracted for, which may reasonably be expected to come into operation by the end of 1917. These new ovens mean an additional ammonia capacity of approximately 156,000 tons of sulphate per year, so that the total will approximate 376,000 tons. Therefore we may safely say that the ammonia needed for the 180,000 tons additional nitric acid capacity required in case of war, is already definitely arranged for, without asking Government support, and will be available at least as soon as a new hydro-electric plant would be.

The transformation of ammonia into nitric acid by the Ostwald or similar process is the only point in which any uncertainty may be said to exist. This uncertainty, however, applies with equal force to the use of the cyanamid process and is equally present in the plan brought forward by Mr. Landis. This uncertainty really consists principally in the fact that the process is not actually being operated on a commercial scale in this country, so far as is generally known, although there is a plant in Canada. It is, however, common knowledge that it is being worked on an enormous scale in Germany at the present time; indeed, it seems impossible to account for their ability to get an adequate supply of nitric acid in any other way. Representatives of advanced methods of ammonia oxidation are, however, in this country, and an efficiency of 90 percent is definitely claimed for the trans-

formation, under guarantee. It would seem that this is the direction toward which government research should be directed, more especially as the process may not prove commercially profitable in peace times, when cheap Chilean nitrate is obtainable.

Reliance upon the by-product coke-oven industry for the production of nitrogen in times of war has an additional advantage that the existing plants are mostly situated at points in the interior which are widely scattered and thus not susceptible to disturbance by enemy attack of any sort. Also, being near the iron manufacturing centers they are located conveniently for use in connection with the production of war munitions.

Reliance upon nitrogen from the by-product coke-oven industry is not advanced as any reason for neglecting the proper development of existing water powers, if this can be done with due regard to the commercial returns that must ultimately justify their existence. In discussing a subject so important as preparedness, it is, however, well to be advised as to all the conditions bearing upon the question, and thus be able to estimate the relative advantages and disadvantages from a broad point of view.

W. S. Landis: The past records of the by-product coking industry, in particular by-product ammonia production, certainly deserves our attention. The by-product coking industry makes as its preliminary product coke, by far the larger part of which goes into the iron industry. The iron industry fluctuates more widely than almost any other industry in this country. A by-product-oven plant is not one that can be economically closed down as demand falls off, for it is the inherent trait of such structures as a by-product oven not to permit a cooling off and heating up a second time. The ultimate limit of by-product production, therefore, is that which will just touch the valleys (minimum outputs) in the iron industry, and with the new ovens under erection and under contract we are very closely approaching that production, beyond which we cannot go for many years to come.

We have not yet developed a domestic use for coke commensurate with that going into the iron industry, and as it is a long and tedious process to teach the public to burn coke we cannot develop this additional consumption for some time.

Up to the present time the by-product industry has been producing ammonia equivalent to 160,000 tons of sulphate of am-

monia per year, and other sources within the United States have been adding practically another 40,000 tons of sulphate of ammonia or its equivalent. In addition to this production in the United States in 1914, the last year for which statistics are available, we imported 83,000 tons of sulphate of ammonia from abroad in order to make up the deficiency in the supply of this form of ammonia alone. As far as the United States is concerned we can assume, therefore, that the normal peace-time requirements of industry in this country cannot find enough by-product ammonia available for meeting their demands, since they have been forced to import up to 90,000 tons of sulphate per year.

Almost 40 percent of the by-product ammonia produced in this country goes into the refrigeration industry. Another 10 percent goes into the chemical and explosives industries. It is, therefore, not safe to assume that we can dispense with all importations of sulphate of ammonia and immediately turn the ammonia product from our coke ovens to the production of nitric acid, even assuming it technically feasible, for the refrigeration industry and mining explosives will play just as important a part in the conduct of war as the manufacture of munitions itself. We must feed our people and our soldiers as well as supply them with powder. In addition we would necessarily be diverting from our fertilizer supply a considerable quantity of ammonia, and we need fertilizers during war as well as in peace. There is no such thing as available coke-oven ammonia for military preparedness, for more of it is consumed in the peaceful arts than we have produced in this country in the past, as indicated by the large importations made from England and Germany. The comparatively small quantity which might be diverted from these peaceful arts without seriously interfering with them cannot be considered by any means a preparedness measure. In other words, the by-product coke industry, to which all due respect must be paid for the important part it plays in our industrial activities, is not, however, a preparedness measure in giving us additional supplies for use in times of war above what we already have use for in times of peace.

John A. Mathews: We have at Syracuse, one hundred and sixty miles from Niagara Falls, about 2,600 kilowatts of Niagara power coming in for use in the electric steel industry, for melting,

and a similar amount elsewhere in the mill. Probably the same amount is used in Lockport and Buffalo. The most striking thing about the development of the electric steel industry is, however, that many of the furnaces which have gone in are not dependent at all on water power. The growth of this industry has been extremely rapid in the last year, and we have now between 100 and 110 electric steel furnaces, either built or contracted for, in various parts of the country from the Atlantic to the Pacific, as far south as Birmingham, Ala., on the southeast and Texas on the southwest. These represent a total tonnage capacity of from 750,000 to 1,000,000 tons a year, depending on the way they are operated. That is about 3.5 percent of the total steel production quoted in one of the papers, and in comparison with crucible steel, with which electric steel is generally compared, it is about five times as great. These furnaces are not all in operation. They represent the use of about 100,000 to 125,000 kilowatts installed capacity. The industry is growing very rapidly indeed, and in fact we have now passed Germany and all other countries in the introduction of electric furnaces, just as in the past we have passed them in the tonnage of Bessemer, open-hearth and crucible steels.

F. A. Lidbury: The members of the Niagara Falls Section of this Society found it necessary to get together to take stock of what I think is not only a serious but a most alarming situation. They found that they had not accurately known what the situation was, that individually they had not realized its importance and that such knowledge and realization on the part of other people was very much less. It was therefore decided to make a careful investigation of the matter, primarily for the purpose of self-education, and we think that these papers show you that we are now in a position to indicate to the country something of what has been accomplished by the use of Niagara Falls power in the electrochemical industry.

We doubt whether a thorough comprehension of that is common even among the members of our Society. We are quite certain that it is not common among the engineering professions, and there is therefore no chance of such comprehension being common in the mind of the public at large. That condition, we

feel, must cease. We think the best thing to do, in the first place, is to lay before the Society as a whole a broad view of what the use of Niagara Falls power for electrochemical purposes has been able to accomplish for the country's industries at large, point out the importance of the matter, point out the situation which at present exists, so that each member of the Society ought to be able to form a center of education among men in kindred professions and among the people with whom he comes in contact.

It is not our purpose to discuss various schemes for obtaining relief from the conditions that now exist. I do not believe it lies within the proper function of this Society to put itself on record as approving or disapproving any particular scheme of water-power development. If we point out what the effects of restriction are, as far as general industry is concerned, as far as they are of general importance to the people, if we do all we can to bring these facts to the attention of the people and of members of legislative bodies, stating merely the facts, not tying ourselves up to any particular program or scheme, then we will have done all we can do, and will have accomplished something which will be more useful than if we attempt to go into the merits of any particular scheme.

Neither is it our intention to cover the whole field of electrochemical industry. Many electrochemical products do not depend in the least on water power derived from Niagara Falls; the refining of copper, perhaps the most important of all, has nothing to do with water power—the location of such plants is decided by other and more important considerations than the cost of power. All that has been attempted in this symposium is to indicate the fields in which Niagara Falls power has succeeded in making this country industrially independent in many important respects.

I do not think it is too much to say that the present state of electrochemical development in this country is due to the fact that when the electrochemical industries (leaving copper refining and such like out of consideration) began to come into existence, there was offered to them at that time a nursery at Niagara Falls which embodied extremely favorable conditions for their growth and for their development. I can easily conceive that in the absence of such favorable conditions at that time, what was prac-

tically a new set of industries might have had its beginning abroad; it was largely because the beginning was at Niagara Falls, in the case of many of these industries, that the growth to a large extent has been at Niagara Falls, and recently from Niagara Falls outwards. That, I think, should be borne in mind.

The passage of two decades since these industries began to come into existence has seen a very considerable change in respect to the desirability of conditions offered at Niagara Falls. Fundamentally this change has been brought about by legislative actions restricting the development of power from the waters of the Niagara River. It may be as well to state the historical course of that restriction. President Roosevelt started the matter in his message to Congress in February, 1906. This was followed in March, 1906, after presumably mature deliberation, by a report of the International Waterways Committee. The Burton Act, passed as an *interim* measure pending the negotiation of a treaty with Canada, received assent June 29, 1906. In 1909 it was renewed. In 1910 the treaty was ratified and proclaimed. In spite of this, the Burton Act, whose limitations were more than the treaty, was renewed in 1911 and finally terminated in March, 1913. Since then the War Department has assumed jurisdiction, and, as has been pointed out to you, the result has been that the limit of 15,600 cu. ft. of water per second for diversion on the American side, imposed by the Burton Act, has been maintained rather than the somewhat more liberal allowance of 20,000 cu. ft. of water per second as allowed by the treaty; as well as the infliction of a momentary peak instead of a daily average.

The only relief which has been experienced through the termination of the Burton Act is the removal, as far as this country is concerned, of the restrictions on the importation of power from Canada. It is interesting to observe that very shortly after the passage of the original Burton Act, electrochemical industries whose products were destined for the American market showed a tendency to locate in other countries. The first important instance of that was the Cyanamid Company of America, which built a plant at Niagara Falls, Ont., in 1910, but their decision to build in Canada was arrived at as early as 1907. I do not think that at that time there was any definite shortage of power on the American side; but the effects of restriction were beginning to appear,

with the result that competitive conditions in the power market were freer on the Canadian side, and consequently prices were then and ever since have been appreciably lower there. The Cyanamid plant uses something like 27,000 H. P.

In 1910 the Norton Company, whose furnace plant was at Niagara Falls, N. Y., constructed a furnace plant in Niagara Falls, Ont., using 5,000 H. P., and substantial additions are being made to this at the present time. In 1911 the Carborundum Company started to operate a furnace plant in France and now has some 10,000 H. P. capacity in France and Canada. The Union Carbide Co. employs, or is about to employ, power amounting to something like 110,000 H. P. in Canada and Norway. The Aluminum Company of America has a plant in Canada, the output of which in normal times goes to some extent into the American market. In fact, all the instances mentioned, with the exception to some extent of the Union Carbide Company's extension in Norway, are dependent upon the American market for outlet. Further, for some time plans have been under way for the installation of a plant at the Saguenay River in Canada to use 250,000 H. P. for the production of fertilizers, again chiefly for the American market. Limiting ourselves to those plants which have already been installed, or whose installation is under way, we thus have already experienced a wandering from the United States to other countries of electrochemical plants of 150,000 H. P. capacity or more. That has been the result, already, of the restriction of power at Niagara Falls.

We come now to the present situation. This is one of extreme famine. Electrochemical companies at Niagara Falls at the present time are either unable to get the power which they require or are finding it extremely difficult. Figures are given in Mr. Edmands' paper showing the extent to which Niagara Falls power furnished in the United States, including that furnished to Buffalo, Syracuse and other towns, is imported from Canada. For a number of years some of us have been wondering what would happen if the Canadian Government saw fit to withdraw the revocable permits upon which exportation of power to this country has depended since 1907. Many people have been inclined to take the view that the Canadian Government would not do anything so unfeeling, so unfriendly. Official expression of that

view is given in a decision of the Public Service Commission of the State of New York for the Second District (Opinion No. 169, of Feb. 12, 1914) in regard to an application for certain rights by a company which wished to import power from Canada and to transmit it through the district from Niagara Falls to Buffalo. In deciding this case, one of the things that the Public Service Commission had in mind was the question of the propriety of capitalizing a contract for power depending upon a revocable permit for exportation under the Canadian law of 1907. This is what the Commissioner says in his decision: "We have nothing before us but the suggestion that the Dominion of Canada may at some future time forbid this exportation. This Commission must assume that international relations affecting so important a subject as the means of continuing great industries which have grown up in reliance upon the use of this important power have become fixed and subject only to such changes as will fully protect the great commercial and industrial interests and rights now served by this power brought from Canada." The immediate result of this service of notice on the Canadian Government that it dare not take away a right granted to companies in the United States was the reduction by a relatively small but noticeable amount of the power for which permits were issued for exportation.

It has evidently, therefore, been unsafe to assume that the power imported from Canada, amounting to a third or more of that utilized, will continue to come over. The unsafeness of this assumption is clearly shown by the fact that within the last few days permits covering the year April 1, 1916, to April 1, 1917, have been issued by the Canadian Government to the exporting power companies, and that they cover substantially *less* power than hitherto. The quantities to be allowed, so I am informed, are:

Ontario Power Company	40,000	K. W.
Canadian Niagara Falls Power Co.	35,000	"
Toronto Power Co.	35,000	"

Further, notice has been definitely served by the Dominion Government that the above amounts are to be reduced by 5,000 K. W. each year; in other words, in about eight years from now no power will be permitted to be exported from Canada. Perhaps

one of the reasons for this action at the present time is that the Canadians realize the difficulties in which the power shortage has placed the American electrochemical companies. It may be that we of the Niagara Falls Section were somewhat foolish to get up and state to one another and to the world in general what the situation was, for the March issue of "Industrial Canada," published by the Manufacturers' Association, contained under the heading, "The Power Famine at Niagara Falls—What is Canada's Interest in a Further Development of Electrical Energy There?" a verbatim report of Mr. A. H. Hooker's paper at the recent meeting of our New York Section, Dr. Landis' paper at the same meeting, and Mr. Tone's paper at the Niagara Falls Section meeting. The following significant comment was added: "After grasping the import of two or three of the addresses delivered at these meetings, which are reproduced herewith, Canadian manufacturers may well ask what interest the Dominion should take in a question which certainly has an international as well as a national aspect. If the United States has reached its limit of production under existing conditions, is there not an opening here for an immediate development by Canada of certain electrochemical industries which will provide a part at least of the chemical products now in strong international demand?" You may well believe that the process of emigration which I have alluded to has not escaped the attention of the Canadians, and that they will leave no stone unturned to accelerate it. That is the meaning, that is the significance, of the present action of the Dominion Government.

We are faced with the situation that not only can the orderly and normal development of the industries which have sprung up around Niagara Falls not continue there, but even their present operations will be seriously restricted unless conditions change in a manner which we cannot at present foresee. What are these industries going to do? Various suggestions have been made, some of them extremely foolish, put out without due consideration. There is, for instance, the statement that the abundant and relatively cheap water powers of the Pacific Coast could be utilized for these purposes. Development of industries to the small extent that the Pacific Coast markets could support might indeed be possible; but we are considering the industries whose

products form the basis of numerous operations in the manufacturing districts of the East. Even if you make the assumption that raw materials are as cheap and accessible on the Pacific Coast as at Niagara Falls, and so forth, a little calculation will show how freight rates to the central area of markets would affect the value of power on the Pacific Coast in the case of electrochemical products manufactured now at Niagara Falls. In the case of about one of these industries, Pacific Coast power might be worth a few dollars per horsepower year; in other cases a minus quantity, usually between — $10 and — $40 per horsepower year. Evidently "around the edges" is not going to help very much, if the edges are so far away.

Many of you know very well that there is an extreme scarcity of developed power in this country in commercially possible situations. Most of the articles produced at Niagara Falls must not only have cheap power but have it in a location from which freight rates to their markets are cheap. In that respect, in normal times, Europe is in a good many cases nearer than the Middle West. It is therefore easy to see why there has been this tendency for these industries to emigrate to other countries, particularly to the country offering available water power in positions nearest to the industrial center of the United States—to Canada.

I think I have stated without any exaggeration what the situation is. I do not want to draw any conclusions and do not want to point any morals. What the people of the country and the legislators must ask themselves in regard to the question of restrictive measures on water power development, particularly on water power development at Niagara Falls, is this: Are we prepared to see these industries, so fundamentally important to us not only in times of peace but to our preparedness for times of war (as the papers you have heard this afternoon so ably and simply show), emigrate to other countries?

I think that about covers the situation. Enough has been said to show you that the purpose of these papers this afternoon is to present no mere academic view of conditions but to point out how electrochemical industries of incalculable importance to the country as a whole are confronted with serious handicaps in their extension and development by a situation already existing which, unless something is done to change it, is bound rapidly to become worse.

J. W. Richards: The late Charles M. Hall remarked to me once that the Horse-Shoe Fall was fast becoming a rapids, that soon there would be only a cascade there. Mr. Edmands' paper points out how, by the suggestion of the electrochemists, instead of the Falls losing its beauty, it can be increased in beauty, while the electrochemist also gets the power he wants. The electrochemist may therefore pose as the prospective preserver of the Falls instead of its destroyer.

E. F. Cone: There is one alloy that Mr. Tone did not touch on with reference to the steel industry, some of which has been made electrolytically at Niagara Falls. That is ferromanganese, which is more important to the steel industry than ferrosilicon, and one in regard to which the country is in more danger from curtailment than is the case with any other alloy, unless it be ferrotungsten. We are directly dependent on England for half the supply of ferromanganese used in this country, and on other foreign countries for a large part of the ferromanganese made in this country because it is smelted from imported manganese ores. I understand that several thousand tons of it was made at Niagara Falls some time ago. Has any process been devised for recovering manganese as an alloy from any slags high in manganese? I understand something of that kind has been done at Niagara Falls.

F. J. Tone: Ferromanganese has been made in the electric furnace at Niagara Falls during the past year in large quantities, but this is purely a war condition made possible by abnormally high prices. Ferromanganese is most cheaply produced in the blast furnace, and under ordinary conditions I do not believe that the electric furnace could compete. I am not familiar with any work on the recovery of manganese from manganese slags.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, held at Washington, D. C. April 27-29, 1916.

POWER DEVELOPMENT—RECLAMATION SERVICE PROJECTS.

By Arthur Powell Davis.[1]

The importance of nitrogen products in the manufacture of explosives and in the fertilization of agricultural lands has been emphasized by the European war in calling attention both to the need of nitrates and to the possibility of the Chilean supply being cut off at any time.

The principal element needed for supplying this need, as well as many other electrochemical industries that might be developed in connection therewith, is a large amount of electric power.

The United States Reclamation Service in the construction of irrigation works has on many of its projects a by-product in the shape of hydro-electric power, usually in blocks too small to be considered in connection with any extensive electrochemical industry, but in a few cases large enough to be thus utilized.

In addition thereto investigation has been made of possible power development for the primary purpose of pumping water for irrigation, and the information thus obtained is interesting in connection with this subject.

POWER DEVELOPMENT ON MINIDOKA PROJECT.

On the Minidoka project in southern Idaho, the Reclamation Service has built a diversion dam which also provides considerable storage and a head of 46 feet upon the wheels of a power plant constructed there with a capacity of 10,000 horsepower. This capacity can be doubled at a reasonable cost.

The power now developed is fully utilized during the summer months for irrigation pumping, and a large amount of power is still available for use in the winter.

Large deposits of limestone are located near one of the pumping plants which a double transmission line reaches, and the avail-

[1] Director and Chief Engineer, U. S. Reclamation Service.

ability of this developed power with convenient railroad facilities is considered one of the most favorable locations for an experimental installation for the fixation of nitrogen.

A further development of 10,000 horsepower could be cheaply made which could be utilized the year around. This region also is within easy reach of one of the largest deposits of phosphate rock in the world, also in southern Idaho, and is hence a convenient point for the manufacture of ammonium phosphate. The coal fields of Utah furnish an accessible supply of coal and coke.

Undeveloped power sites along the Snake River in the same region could be made to produce several hundred thousand horsepower for eight or ten months in the year.

Minidoka power house.

POWER DEVELOPMENT ON THE BOISE PROJECT.

In Idaho the Reclamation Service has built a high masonry storage dam about 240 feet above the river bed. More than 1,000,000 acre feet of water have to pass this dam site every year, all of which is used for irrigation in minimum years, but in ordinary years there is considerable surplus.

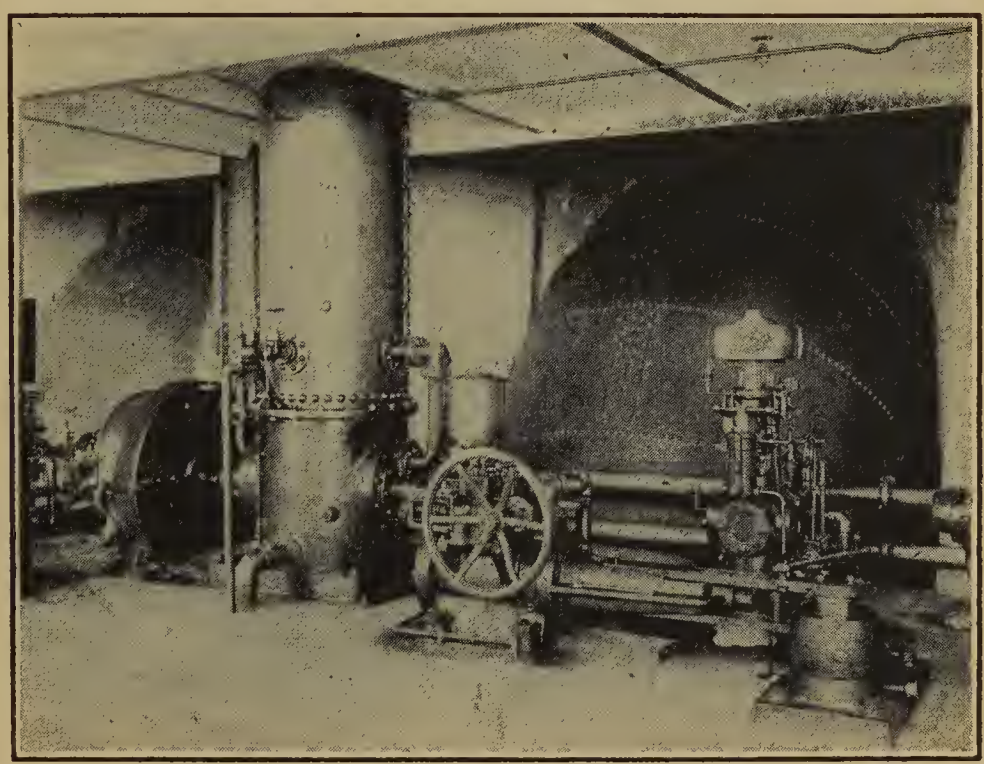
Power development at this dam could utilize the head in the reservoir which varies from 60 to 230 feet. The quantity of water available during the summer would be about 5,000 cubic feet per second, which would be diminished in the spring and fall, and in the winter only about 200 cubic feet per second could be drawn.

Provision has been made for the convenient installation of power to the extent of 17,000 horsepower at this site. A greater amount could be developed during the summer if found desirable.

PATHFINDER DAM, NORTH PLATTE PROJECT.

The Pathfinder Dam on the North Platte River is 210 feet high, forms a reservoir of 1,100,000 acre-feet, and intercepts an annual flow which varies from 1,000,000 acre-feet to over 3,000,000 acre-feet. The water of low and average years is all required for irrigation. It could be utilized for power as it comes from the reservoir, but would be available only six or eight months of the year, and the head would vary from 60 feet to 200.

The site is 55 miles from the railroad, and the highway is both hilly and sandy. Although plentiful deposits of limestone, sand, and soda are near, there has been no power development.



Interior of Minidoka power house.

POWER AT ELEPHANT BUTTE DAM, RIO GRANDE PROJECT.

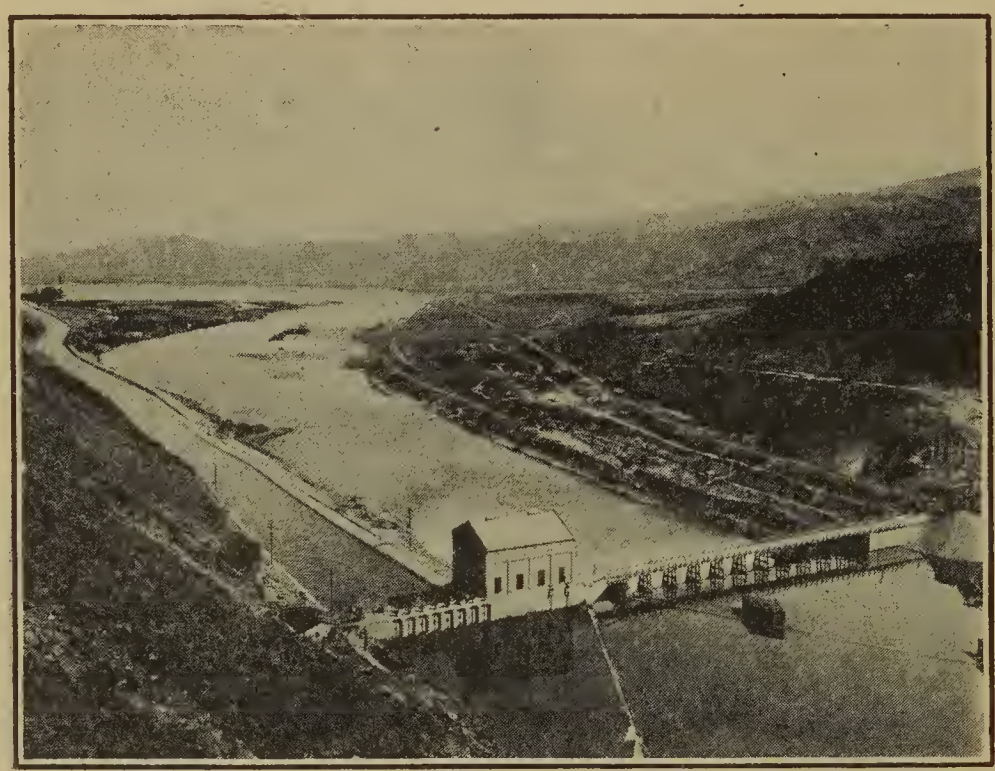
A large amount of power is available during the irrigation season at the Elephant Butte Dam, but usually during two or three months of the winter no power is available.

The power is to be developed by using water drawn from the reservoir as needed for irrigation under the available head in the reservoir at the time drawn. The available head will vary from 65 to 185 feet, and the maximum quantity of water drawn will be about 2,500 cubic feet per second. During eight months of the year it would be possible to develop from 20,000 to 30,000 horse-

power, according to the head available and the quantity of water needed for irrigation.

The development of power was considered in designing the dam and six 5-foot power outlets were installed. The maximum output from these would amount to 12,000 horsepower. An 8,000 horsepower plant has been estimated to cost about $420,000.

The construction of a hydro-electric plant for commercial purposes would be unattractive, as a large steam auxiliary would be required in order to operate in the winter when no water is drawn from the reservoir. The feasible power development, however,



Boise power house.

is well adapted to the needs of pumping for irrigation for which market exists within feasible transmission distance. Limestone is plentiful not far from the dam and coke is obtainable from the mines of northern New Mexico.

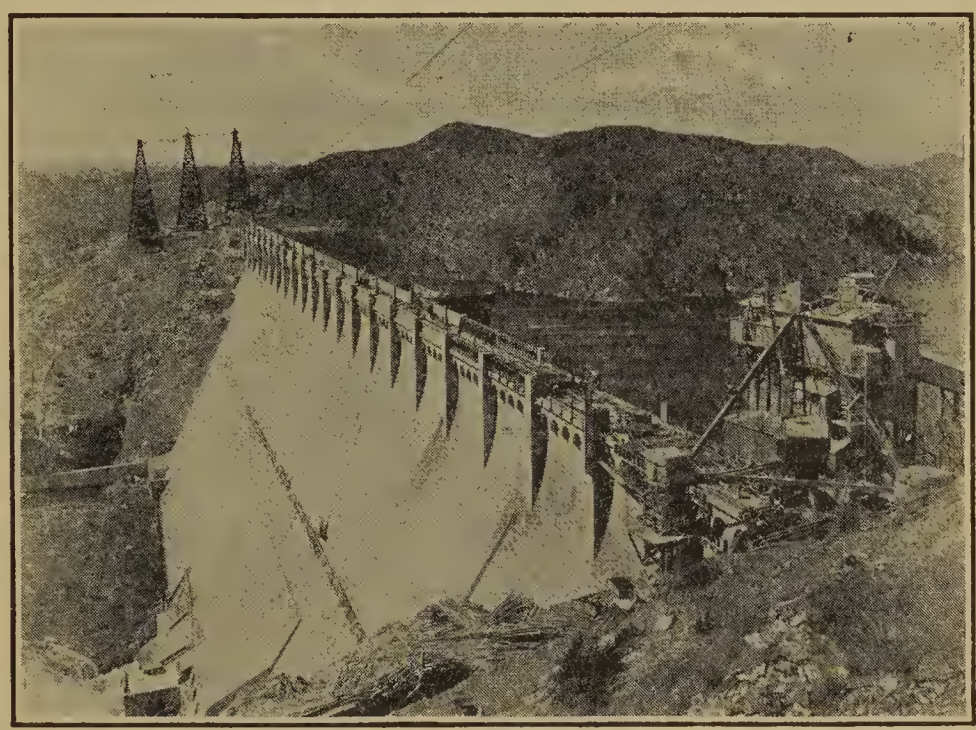
SHOSHONE PROJECT POWER DEVELOPMENT.

On the Shoshone project a masonry dam has been constructed in the canyon of the Shoshone River about 250 feet above the river bed. This dam furnishes a storage reservoir of about 450,000 acre-feet capacity and water is stored primarily for irrigation purposes. The flow of the stream, however, when thus regulated is greater than required for the irrigable lands and will

furnish a surplus of water which can be used for power purposes during the winter.

The river falls rapidly below the damsite, and it is easily feasible to develop power varying from 25,000 horsepower in winter to 40,000 horsepower in summer of average years.

In the immediate vicinity there is an unlimited supply of limestone, and a few miles below the power site is a large deposit of native sulphur. Farther down the valley and also in other parts of the State of Wyoming are large and easily accessible deposits of lignite, all of which can be made useful in various electro-



Pathfinder Dam, North Platte.

chemical industries. There are also considerable deposits of phosphate rock in the State of Wyoming which could be brought in by rail and used in connection with the process for the manufacture of ammonium phosphate as a fertilizer.

With a high dam and a large reservoir already constructed, together with the proximity of limestone, sulphur, coal, and phosphate rock, the Shoshone location constitutes one of the best localities for the establishment of electrochemical industries on our projects.

IRON CANYON POWER DEVELOPMENT.

The Reclamation Service has made an investigation of a large water storage and irrigation project at the head of the Sacramento

Valley, which contemplates the storage of water by means of a high dam at Iron Canyon, not far from the city of Red Bluff, Cal.

Various alternatives and possibilities were considered, all of which provide for a dam with excellent opportunities for power development. The quantity of water available would vary from 3,700 second-feet to about 5,000 second-feet, and the head would vary from 60 feet up to 130 feet, furnishing from 25,000 to 35,000 horsepower output at the switchboard. The large storage reservoir available makes this power very desirable as a by-product of works constructed primarily for irrigation. Convenient railroad transportation adds to its value for power and irrigation.

This reservoir has also an important bearing on the flood control problem, and there is opportunity to furnish important contribution to the control of the flood water of the Sacramento River which is sometimes very destructive. The total cost of the most comprehensive plans considered will be in the neighborhood of $16,000,000.

It is estimated that by proper manipulation of the storage reservoir at Iron Canyon, a reduction in the cost of protective work proposed for the control of the floods of the Sacramento below this point may be made of about 50 percent in the upper end to perhaps 10 percent in the lower end of the river system.

POWER DEVELOPMENT ON FLATHEAD RIVER.

Large power possibilities exist near the outlet of Flathead Lake, and preliminary studies have been made of the development of power in this vicinity. The flow of the Flathead River is rarely less than 4,000 second-feet, and this can be increased to 10,000 second-feet by the construction of a dam in the Flathead River below the outlet of Flathead Lake, converting this into a storage reservoir. Such a dam would produce a head of 240 feet and make possible the development of from 200,000 to 300,000 horsepower. So large a storage as this, however, is handicapped by the ownership of land around Flathead Lake which would make damages very large, but a moderate regulation would develop a large amount of power. There are several other power sites on the Flathead River which would utilize the same water and large power developments could be located there.

COLUMBIA RIVER POWER POSSIBILITIES.

The Reclamation Service in co-operation with the State of Oregon conducted an elaborate investigation in 1914 of the power and irrigation possibilities which could be developed by the construction of a dam in the Columbia River at what is known as "Five Mile Rapids," near The Dalles, Oregon.

At this point the Columbia River channel suddenly reduces from a width of about 1,800 feet to a width of only about 150 feet and continues between two rock walls in a very narrow and deep channel. The plan is to build a dam at the narrow neck where the river first enters this narrow gorge, construct a power canal, and erect a power house at a point about 1½ miles below the dam site. The quantity of water available varies between 50,000 second-feet minimum and 1,000,000 second-feet maximum. The head for plant operation will vary from a minimum of about 45 feet to 105 feet maximum. The power which could be developed continuously 24 hours per day and 365 days in the year will aggregate about 480,000 electrical horsepower, with the possibility of the development of additional large blocks of power for a part of the year. It is estimated that this project would cost about $50,000,000. The secondary power possible to develop is as follows (this is in addition to the primary power of 480,000 horsepower):

	Horsepower.
11 months in the year	120,000
10 months in the year	220,000
8 months in the year	320,000

It has been proposed to use this power for irrigation by pumping, in the smelting of ores, in electrochemical processes, etc.

PRIEST RAPIDS POWER DEVELOPMENT.

At the Priest Rapids, on the Columbia River above the mouth of the Snake River, an average head of 60 feet can be obtained, with which, with the minimum discharge of the river of about 40,000 cubic feet per second, over 200,000 horsepower can be developed the year around.

Fifteen or twenty percent of this power could be used during the summer for irrigation purposes, but as the summer water supply is higher than the winter, the amount would be about the same the year around.

Good river navigation is available for bringing the needed limestone.

The above brief description will give a general idea of the possibilities of power development on the Reclamation projects. Whether such development would be commercially advantageous for the production of nitrogen from the atmosphere is, however, a question which depends upon numerous factors, such as the amount of power possible to be produced at an individual plant, competition with the relatively cheap water power of the East, freight rates, etc.—a question which can be answered only after an exhaustive study of the entire situation. It is to be hoped that the preparedness program will include this study of a question which is of such vital importance to the welfare of the United States.

A lecture presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27, 1916, Mr. John H. Finney in the Chair.

THE NECESSITY FOR WATER POWER DEVELOPMENT.

By Henry J. Pierce.

It is a strange fact that the proportion of our total available water power thus far developed is only about the same as was the proportion of our agricultural lands under cultivation one hundred years ago, at which time the development of our natural resources had not been commenced. Today, while practically all the farming lands of the United States, with the exception of the arid portions of the West, have been brought under cultivation, and while such great natural resources as coal, oil, phosphate and minerals have been developed as rapidly as necessity required, yet but 10 percent of our available water power has been utilized.

Up to 1885, when electricity first came into use for practical purposes, the use of water power was limited to the turning of wheels for operation of a few grist mills and other manufacturing establishments. During the thirty-year period between 1885 and 1915, 6,000,000 H. P. was developed out of a total available amount of 61,678,000 H. P. As the principal use for electric energy has been the operation of public utilities, the water powers thus far utilized have been those located at points nearest large centers of population, though in some instances power is being economically transmitted in large quantities for distances of from 150 to 200 miles.

The total available water power of all countries of Europe combined is 35,965,000 H. P., the development of which is rapidly progressing.

While we are at present but upon the border land of the electric age, yet the problems consequent upon the generation, transmission, transformation and utilization of electricity are practically solved, and only a larger supply at lower cost is necessary to make its use almost universal. The average requirements of each inhabitant of the United States for heat, light and power

are, roughly speaking, the equivalent of 13 H. P. hours per day to provide for his or her needs in heating, cooking, lighting, manufacturing, transportation and allied service. The people of the United States have come to exercise a nice discrimination between existence and living, and demand not only the necessities but a measurable part of the comforts and luxuries of life. Power and machinery afford the best supplementary means to this end yet devised, and the wonderful agency of electricity has become man's most popular, reliable and capable servant in doing the world's work.

Three great principal uses for electric energy await the development of our water powers:

The operation of pumping plants in connection with irrigation projects;

The electrification of railroads;

Certain manufacturing purposes, such as production of atmospheric nitrogen, fertilizers, explosives, electrochemicals, wood pulp, paper, iron, steel, etc.

IRRIGATION.

It is estimated that there are at least 10,000,000 acres of arid lands located in the Far Western States, lying above the reach of gravity water, that can only be reclaimed through water raised by pumps operated by the cheap hydro-electric power now latent and wasting in the various streams from which the water would be pumped. Thus the land, and at a lower level the water to irrigate it, and the power to raise the water to the land are often all assembled at one point. Given water, these lands will produce every fruit, vegetable and grain that is native to the temperate zone, and are capable of supporting a population of 2,000,000 people. If capital can be safeguarded, it is safe to say that hundreds of thousands of water horse-power will be utilized within the next ten years in connection with the reclamation of arid lands, and that in addition to what the Government service will accomplish, hundreds of millions of dollars of private capital will be used for establishment of reclamation projects in connection with pumping plants. Lands are being irrigated in 27 States, and as far East as New Jersey and Florida, and two Western States have now nearly 5,000,000 acres of land under irrigation.

ELECTRIFICATION OF RAILROADS.

Four hundred and fifty miles of the main line of the Chicago, Milwaukee & St. Paul Railroad, being the portion between Harlowton, Mont., and Avery, Idaho, is now being equipped for operation by electricity, and about one-half of this mileage has already gone into successful operation. Quoting from the testimony given before the Senate Public Lands Committee in 1914, by John D. Ryan, a director of the Milwaukee Railroad, and also president of the Montana Power Company, which will furnish the power:

"The railroad will pay under the contract for power delivered over 450 miles of its road something like $550,000 a year. It is paying now for coal to operate its steam trains over the same line approximately $1,750,000, and they furnish their own coal from mines on their own road, and one-third of their equipment is used in hauling coal to themselves, whereas with electric power there is not any such waste."

Mr. Ryan testified that the Butte, Anaconda & Pacific R. R. are paying $96,000 per year for electric energy to operate 80 miles of road, as against a former cost for coal of $270,000, a saving of $174,000 annually.

Thus, the year 1916 marks the dawn of the Electric Era in railroading and the accomplishment of one more step along the lines of true conservation through the saving of coal and the utilization of wasting water powers.

In view of the great economical success of the electrification of 450 miles of the Milwaukee line, it is almost certain that within the next ten years a majority of the railroads operating through the mountainous country of the Far West, where hydro-electric power can be developed cheaply, will adopt electricity as motive power. Forty-eight thousand seven hundred miles of railroad are now being operated in the States of Washington, Oregon, California, Idaho, Montana, Wyoming, North Dakota, South Dakota, Utah, Arizona, Colorado and Nevada. It is estimated that 10,000 H. P. is needed to operate 100 miles of single track, and therefore it will require 4,870,000 H. P. to electrify all of the railroads of these States, or one-ninth of the total hydro-electric power possible to develop in the territory traversed by these rail-

roads. A great portion of the trackage is over mountain divisions, and the use of electricity in place of coal will result in great economy of operation, obviate the danger of forest fires, and by elimination of noise, smoke, gas and dust, and through a more generous ventilation which will be possible when the flying cinder need no longer be taken into account, will make travel far more safe, comfortable and pleasant than at present. The wood-burning locomotive of fifty years ago weighed twenty tons. The electric locomotive of today is 112 feet long and weighs 285 tons. These wonderful motors absorb the mechanical energy of the train going down grade by gravity and return it in form of electrical energy to substations for use by trains running along the level or going up grade. Thus, through regenerative braking, from 25 percent to 52 percent of the power is recovered.

PRODUCTION OF FIXED NITROGEN.

The greatest need for the development of our water powers is the imperative necessity, and it is a national necessity, that sufficient fixed nitrogen should be produced within the boundaries of the United States to meet its requirements. Nitrogen comprises four-fifths of the atmosphere and is a constituent of all organized life and tissues. It is a colorless, tasteless, odorless, gaseous, non-metallic element. We live in it, we breathe it, we eat it and it constitutes a portion of our human frame. It is absolutely necessary to the existence of animal and plant life. Without fixed nitrogen the earth would soon become an uninhabited desert waste. While the atmosphere contains an exhaustless supply of nitrogen, it being estimated that 20,000,000 tons exist above each square mile of the earth's surface, yet 90 percent of the plant life that lives in it does not absorb it, and the remaining 10 percent absorbs but a small porportion of that which it requires. The world has been dependent for most of its supplies of fixed nitrogen upon the nitrate of soda beds of Chile, where, during some convulsion of nature at some remote past time, the soda absorbed quantities of nitrogen from the air. During 1913 the United States imported 625,000 tons of Chilean nitrates, valued at $21,000,000, upon which the Chilean export duty was 60 percent. We thus paid to the Chilean government $7,500,000, which may be considered merely a part of the amount

which the people of the United States pay for its policy of water power stagnation. In other words, the people of this country would be quite as well off as they now are if they granted a subsidy or bonus of $7,500,000 per annum for the establishment of the water power nitrogen industry in the United States. In the past thirty years, export tax on nitrates has netted the Chilean government about $500,000,000. The richest nitrate beds of Chile, however, will be practically exhausted by 1923, and were it not for the most wonderful of all modern discoveries, whereby it is now possible with the aid of electric energy to obtain a supply of fixed nitrogen from the atmosphere, the world would stand in imminent, deadly peril, the perpetuation of the human race would be endangered, and we would be in a position similar to that of a shipwrecked sailor drifting on an immense ocean of brine but dying for lack of water. It is a wonderful Providence that perpetual and inexhaustible supplies of nitrogen may be obtained from the atmosphere by the use of electric energy obtained from our water powers whose flow is also everlasting, and that thus the limited supplies of coal and other fuels laid aside by nature may be conserved for other uses. The Governmental paralysis imposed seven years ago upon the development of water powers in the United States, through the restrictive interpretation of Federal laws, still continues; but that period has been one of great hydro-electric development in Europe, where over 1,200,000 water horse-power has been utilized for the extraction of nitrogen from the atmosphere, being over three times the quantity of power produced at Niagara Falls, while the United States, out of 61,000,000 H. P., is not using a single horse-power for that purpose. Hydro-electric nitrogen plants have been established in Norway, Sweden, Germany, Australia, Italy, Switzerland, France, Spain, Japan and Canada, but none in the United States. The nitrogen industry of Europe represents an aggregate investment of over $300,000,000, employs 50,000 people, and the annual value of its products and derivatives is upward of $220,000,000. In Germany, where practically all the water powers have been developed, a nitrogen plant is being built which will use 100,000 H. P., to be produced from cheap coal. England is seriously considering the development of 1,000,000 water horse-power in Sweden and Iceland to provide for her future supplies

of nitrogen. Thus, with a foresight that is a reproach to our intelligence and enterprise, these other countries are insuring their requirements of this great human necessity against the time when it will be no longer possible to obtain supplies from Chile. It seems incredible that nothing has been done thus far toward the establishment of the nitrogen industry in the United States. Several years ago an effort was made to locate an atmospheric nitrogen plant upon the Coosa River in Alabama where a large water power would have been developed, and near which were ample supplies of the necessary raw materials, high-grade limestone and cheaply mined coking coal. The plant, moreover, would have been located in the center of the cotton belt where the most of its product would have been marketed in the form of fertilizer. As development capital could not be obtained under our restrictive Federal water power laws, a bill was introduced in Congress to meet the requirements of the case, but failed to become a law, and, as a result, the plant was established at Niagara Falls, Canada, where a contract was obtained for electric energy at a low figure, and the capacity of this plant has been increased sixfold in five years. As a result, the United States has lost and Canada has gained a great manufacturing institution, covering an investment of millions of dollars, and the farmers of Alabama are paying the freight on its product from Canada to their cotton fields. It is estimated that an investment of $860,000,000 would be necessary to produce mechanically from the atmosphere as much nitrogen as Chile's nitrate deposits yield every year, and this shows the enormous possibilities for the future contained in the establishment of this entirely new industry in the United States.

The two largest and most necessary uses for nitrogen are in connection with the manufacture of electro-fertilizers and explosives.

ELECTRO-FERTILIZERS.

Seven million tons of fertilizer valued at $170,000,000, were sold in the United States during 1913, and for its manufacture over $40,000,000 of nitrogenous and other material was imported, most of which could have been made in this country, with the aid of electricity. The average amount of fertilizer used in

the United States is 28 pounds per acre of cultivated lands, against 200 pounds per acre in Europe, with the following results:

Comparison of average yield per acre in bushels of crops in the United States and Europe:

	Wheat	Oats	Barley	Rye	Potatoes
Europe	32	47	38	30	158
United States	15	29	25	16	96

In twenty years Germany has, through the use of fertilizer, increased the average of all crops three and one-half times as much per acre as America. Germany, with 70 percent of the population of the United States and cultivating but one-fourth the area, grows 95 percent of the food products which she consumes.

If our use of fertilizer had been equal to one-half of that of Europe per acre in 1913, 24,000,000 tons would have been required, of the value of $580,000,000, and in the production of which 12,000,000 water horse-power must have been utilized, and the resultant increase of crop value would have exceeded $2,000,000,000.

Careful and extensive experiments made in Germany have shown that by the addition annually of 150 pounds of nitrogen per acre, crops of rye, wheat, oats, barley and potatoes are more than doubled, and the reports of the German Agricultural Department show that as the result of feeding the soil with 2,000,000 tons of nitrates the increase of crops amounted to 63,000,000 tons. These figures show how important is the rôle actually played by nitrogen in the cereal production of Europe. The German farmer who pays but one-half as much for his fertilizer as does the American farmer, practically uses his land as an agent for transforming fertilizer into product, while the American farmer tries to get products out of his starving land without feeding it sufficient plant food. The American people are falling far behind the rest of the civilized world in the most important of all human activities, the cultivation of the soil. European nations waste nothing, and in many clever ways create values out of what we discard as worthless. Our comparatively young country is wasting its resources with terrible profligacy, as is evidenced by our using up our stores of coal and oil instead of utilizing our wasting water powers.

The crops harvested annually in the United States abstract over 1,000,000 tons of nitrogen from the soil, and as the world's supply of combined nitrogen is increased only slowly and in small degrees by nature, the soil of farmed lands is entirely dependent upon fertilizer for replenishment of the stock of nitrogen which it gives up in its yield of crops.

At the agricultural station at Rothamsted, England, wheat has been grown year after year, on the same land, for sixty-three seasons, without fertilizer, with an average crop return of twelve bushels per acre, while during ten years the average crop on adjacent plats of ground receiving plant food each year was forty bushels per acre.

The present method of manufacture produces a finished product containing but 12 percent of active fertilizer, and 88 percent of utterly useless material, on which freight and haulage must be paid by the farmer; whereas, the electro-fertilizer product contains 60 percent of fertilizing material. By the electric process not only is nitrogen obtained from the atmosphere, but phosphate rock may now be treated by electricity, instead of sulphuric acid, for extraction of phosphoric acid.

It is estimated that fully 10,000,000,000 tons of phosphate rock, containing an average value of 70 percent, is located in Idaho alone. Phosphorus is an essential constituent of flesh and blood and bone and brain. How essential it is has been clearly shown by experiments recently made by the Wisconsin Experiment Station. Animals fed with a ration deficient in phosphate thrived for a time and after three months collapsed. In an immature state some of them were killed and it was found that the flesh was taking the phosphate from the bone in order to supply its need. This went on until the bones were no longer able to supply phosphate to the flesh and the collapse came.

The use of fertilizer has a most intimate relation to the cost of living, which has increased in this country at a much more rapid rate than it has abroad.

The population of the world doubles in sixty-five years, and with increase in numbers there is an increased per capita consumption of food.

The extraordinary increase in the cost of living in the United States has been principally in the cost of food products, while

other items than foods have increased at only the general rate prevailing throughout the world. From 1900 to 1910 the cost of foods in the United States increased 35 percent, and abroad only 15 percent. While our population increased 21 percent during those ten years, crop production increased only 10 percent, and our exportation of wheat and flour decreased from 31 percent to 13 percent of the amount produced. The rapid increase in food cost in this country can only be checked by increased crop production, just as food prices are held down in Europe through increase in yields per acre obtained without additional labor through the use of fertilizer. The countries of highest agricultural development are the largest consumers of fertilizers.

The less nitrogen there is available as foodstuff, the nearer the population is to starvation. The great famines in such nitrogen-deficient countries as India, China and Russia are sad but striking examples of nitrogen starvation.

The mutterings of strife for commercial supremacy between England and Germany were heard as far back as early in the nineteenth century, when the value of bones as a plant food becoming realized, the great German chemist, Liebig, was moved to say:

"England is robbing all other countries of their fertility. Already in her eagerness for bones she has turned up the battlefields of Leipsic, of Waterloo, and Crimea. Already from the catacombs of Sicily she has carried away the skeletons of many successive generations. Annually she removes from the shores of other countries to her own the manurial equivalent of three and one-half millions of men."

EXPLOSIVES.

Nitrogen, in the form of nitric acid, is the principal constituent of explosives, such as gun cotton, dynamite and smokeless powder. The basis may be glycerine, wood pulp, cotton or a coal tar product, but in every case nitric acid is the agent used to transform inert substance into powerful explosives. Modern warfare today means nitric acid. What use are men and guns without powder? Powder today has the significance in war that it has never had before. Today a battlefield as to attack is the playing of a sheet of metal at such velocity and in such volume

that it sweeps clear to the underlying rock everything within reach and is like a hose playing a leaden stream. The whole thing means powder and there is no such thing as powder without nitrogen.

We are annually producing about 250,000 tons of explosives valued at $40,000,000, and we pay $23,000,000 for the raw materials that enter into them, most of which are imported. Had it not been for the discovery of the nitrate fields of Chile, the explosive industry, as it is known today, would have been impossible; and, as coal and minerals could not have been mined without the use of explosives, the development in mining and transportation, which has characterized the last half century, could not have been made.

In case of war, we would be almost entirely dependent upon foreign nations for our supply of nitrogen for manufacture of powder, and would be practically defenseless unless we could obtain it from other nations. If the country with whom we were at war should be strong enough to seize the nitrate deposits of Chile, or to prevent shipments to this country, it would leave us helpless, in spite of our 100,000,000 of people and our army and navy. We would be forced to commandeer all sources of nitrogen, including fertilizer, and it might come about that some of our agricultural regions could no longer be devoted to food production, even though the scene of conflict never penetrated to them. The War Department is greatly concerned over this weak point in our national defense, and writers who are authorities upon the subject, from the military standpoint, urge the immediate development of our water powers, and establishment of atmospheric nitrogen plants, in order to ensure the production of our requirements of nitrogen within the borders of our own country; and they strongly recommend that the nitrogen plants be so strategically located throughout the country as to be reasonably well protected against attack, in case of foreign invasion.

Franklin K. Lane, Secretary of the Interior, in his last annual report, under the poetic and beautiful caption "Turning Water Into Power," says:

"Then, too, there is that mystifying miracle of drawing nitrogen from the air for chemical use, which can be done only with great power, but is being done in Germany, Norway, Sweden,

France, Switzerland and elsewhere; by which an inexhaustible substitute for the almost exhausted nitrates of Chile has been found. To increase the yield of our farms and to give us an independent and adequate supply of nitrogen for the explosives used in war, we must set water wheels at work that will fix nitrogen in lime."

General William Crozier, Chief of Ordnance, U. S. Army, said in his last annual report to the Secretary of War:

"I do not know of any article which, at the present time, should cause more concern with reference to the war-time supply than should nitric acid. The nitrogen in the nitric acid is obtained from sodium nitrate, which comes from Chile, and the country is therefore dependent for its powder manufacture upon Chile."

A recent statement showed that the stock of powder for small arms in possession of the War Department amounted to 200,000,000 rounds, which would only be sufficient in time of battle to last an army of 500,000 men eight days; further that there is only sufficient ammunition on hand to fire all of our coast defense guns forty times, or continuously for about one hour. The War Department has, for some time, been accumulating a stock of Chilean nitrate to provide for emergencies; but in time of war, it would produce only sufficient explosives to last for a short period of time. Germany is shut off from supplies of Chilean nitrate for powder making, and if she had not developed her water powers for the purpose of obtaining nitrogen from the air, the European war would be ended today and Germany beaten. But the Germans are operating all their nitrogen fixation plants on a war basis, and thus are enabled to manufacture a plentiful supply of ammunition.

MANUFACTURE OF PAPER AND WOOD PULP.

One-third of the cost of manufacturing wood pulp and paper consists of the cost of power. The imports of these articles into the United States are growing at an enormous rate. Sweden and Canada have been developing their water powers, and hence it is interesting to note the exports of wood pulp and paper from those countries to the United States:

	1911	1912	1913
From Sweden.....	84,378 tons	107,884 tons	130,693 tons
From Canada.....	83,856 tons	131,412 tons	281,586 tons

With the production of cheap electric energy, through the development of our water powers, the pulp and paper industry will come back to its own in the United States. It is inevitable that the industry must spread westward, and that through the utilization of the water powers and the forests of the Northwest, these imports of wood pulp and paper will be displaced with products made in our own country.

MANUFACTURE OF ELECTRO-METALLURGICAL PRODUCTS.

While coal, coke and gas are principally used in the smelting and refining of iron and steel, and while one-fourth of the entire world's output of coal is used for that purpose, yet in 1913, 668,000 tons of steel were produced in Europe and 165,000 tons in the United States, through the use of the electric furnace.

The Iron Trade Review calls attention to the extraordinary expansion in manufacture of electric steel during the past eighteen months, during which period the production has trebled and is now almost as great as crucible steel. The new industry has come to stay and will expand most rapidly in the localities where water power is abundant and can be harnessed cheaply. In Alabama and Tennessee practically inexhaustible deposits of iron ore and limestone are located in the vicinity of great undeveloped water powers, and now that the problem of making pig iron through the use of cheap electricity is practically solved, the South is bound to become in the not very distant future, the center of the metallurgical industry.

Students of the question believe that the use of cheap hydro-electric power, in the making of iron, will eventually bring about a commercial revolution in the leading nations. The United States, Germany and England produce seven-eighths of the word's iron. Germany has already developed practically all of her water powers, England has but few, and the production of iron would, therefore, under these circumstances, pass into the hands of the United States because of its water powers and it would become omnipotent in the production of iron and steel. In fact, these authorities believe that all industries which consume large amounts of mechanical energy will be forced to emigrate to countries where water power is abundant.

MANUFACTURE OF ELECTROCHEMICALS.

Over 200,000 homes are lighted by acetylene gas, produced from calcium carbide, in the manufacture of which, at Niagara Falls, great quantities of hydro-electric energy are used. Because of our restrictive water power laws, the American Carbide Company could not increase its production in this country, and is now building a plant on the seacoast of Norway, where it has contracted for the delivery of 80,000 h. p., developed from water power, and expects to ship most of its product to the United States.

The aluminum industry now uses 300,000 hydro-electric horsepower in its various factories, and is developing additional water powers which will in the near future bring the total to fully 450,000 horse-power.

Electrochemical products were reported by the last census to be made in thirty-four establishments at Niagara Falls of a value of $18,450,000 per annum, consisting of abrasives, electrodes, calcium carbide, caustic soda, chlorates and such metals and alloys as aluminum, silicon, ferro-vanadium, etc.

If all the water at Niagara Falls were utilized it would be possible to generate 5,000,000 h. p. The American and Canadian Governments permit the use of sufficient water to generate 400,000 h. p., all of which is in use, and an 80,000 h. p. steam plant, to be operated by coal, is being built on the shores of the Niagara River to provide for further demands for power.

There are many other large and constantly increasing uses for hydro-electric power which can not be enumerated here for lack of time.

Every encouragement must be given to manufacturers who use large quantities of hydro-electric energy if they are to be enabled to locate their factories in the United States and compete with the cheaply developed water powers of Europe and its cheap labor. As an example, at Thelemaken, Norway, where the water formerly flowed over a cliff into the sea 300 feet below, most of it is now diverted and a great quantity of cheap power produced. One can stand at the edge of the cliff at this waterfall, and look down into hatches of a ship floating in 60 feet of salt water. The nitrogen plants of Europe are all operated on a basis of 60 cents per day

for ordinary labor of a class that would cost two dollars per day in America.

With the abolition of our present faulty laws, and the enactment of practical legislation, great water power developments which have been held back for years, would be undertaken on the Connecticut River, where the power would be used in operating the mills of New England; on the Tennessee and Coosa Rivers of the South, in connection with the manufacture of fertilizers, iron and steel; on the upper reaches of the Mississippi for public utility uses, and on the Columbia, Snake and Pend d'Oreille Rivers of the Northwest for irrigation and manufacturing purposes. Through installation of power dams and of locks, these rivers will be made navigable for an aggregate of hundreds of miles further into the interior of the country, and this broad-visioned development of inland waterways would be accomplished by private capital, without a cent of cost to the people, through Government taxation.

But while an enormous amount of water power is latent in our navigable rivers, a far greater amount exists in the non-navigable streams flowing through the public lands and Federal reserves located in the far Western States. Here nature has segregated her natural resources; the thirsty land awaiting irrigation with the water containing the latent water power washing its shores; the forests necessary to manufacture of wood pulp and paper lining the banks of the falling water; the limestone and phosphate needed for fertilizers and explosives located contiguous to wasting water powers.

THE REASON WHY OUR WATER POWERS ARE NOT BEING DEVELOPED.

Every one agrees that the sole reason why our water powers are held back from development is because Congress has failed to provide suitable legislation permitting their development.

It seems almost unbelievable that an enlightened Government like ours should not only fail to encourage, but should blindly bar the way to, the development of a great natural resource so important to the farming and manufacturing interests of the country, and so necessary to national safety. The fault is not with private enterprise. As has been shown, Americans have repeatedly tried, but in vain, to get the right from our Government to establish

hydro-electric plants upon navigable streams or within the Government domain upon fair and equitable terms that would justify the risk and the large expenditure of time and money involved, while fully protecting the public interest.

They have been met by impracticable conditions which no prudent man could agree to. Prevented by the laws and policy of their own country from engaging in developing a great natural resource of incalculable value to any country possessing it, they found in other lands the welcome for their enterprise and capital denied to them at home. And so Canada and Norway are now enjoying the advantages of American energy, enterprise and capital in the successful establishment and operation of great manufacturing plants involving an expenditure of many millions of dollars and giving steady employment to thousands of men.

The production of hydro-electric energy is a hazardous business. Cost of installation is difficult to determine in advance, and often costs more than anticipated. Floods sometimes destroy dams and power houses, and yet men of business and of technical and scientific experience, who have made hydro-electric development their life work, as well as manufacturers of all of the great products for which the hydro-electric energy would be used, stand ready to undertake the development of our now wasting water powers and the other vast commercial features connected with it as soon as our present impossible Federal laws are corrected to a fair business basis, under which practical men will give their time and capital will invest.

The internal development of a country must precede its external commerce. In every one of the twenty years ending with 1913, the foreign commerce of Germany has exceeded that of the United States, and the excess has been steadily growing greater. For the single year 1912 it was $853,000,000, and for the whole twenty years it was $7,700,000,000. There is nothing in that record for the United States to be proud of, even if the two countries stood somewhere near on equality. But we have an area seventeen times as great; we have 30 percent more population; we have nearly three times the accumulated natural wealth, and our natural resources are twenty times greater than those of Germany.

Then why not give those who would develop our wasting water powers the right to work, the right to build and expend and

develop, the right to help create a greater and more powerful industrial nation? Why not give them a law to work under which shall encourage and not hamper their just activities?—a law which, while placing them under the constant supervision of the public authorities, and sufficiently safeguarding every public interest, yet shall be of such a fair and businesslike nature that under its operation men may hope for a generous return for their work and risk, and capital be assured of a safe investment. This done, they will open up deserts and make farms; they will build factories and cities; open up new reaches of inland waterways; employ labor, and reduce the cost of living. The result of the passage of broad, wise and not too restrictive water power laws by the present Congress will be all to the good and nothing to the bad.

Reasonable, sensible, practical regulation safeguarding the public interest no one objects to. The trouble is that the Federal policy covering the use of water power is so narrow, so full of restrictions, so loaded down with conditions that no prudent man will venture to embark in the business.

There are some who would place a Federal tax upon water power. Coal and oil used to produce power are not taxed, then why tax turning water into power? Why place burdensome legislative restrictions upon developments so necessary to the advancement of the Nation?

The belief that any law that Congress may enact will be eagerly accepted by would-be water power developers and the investors upon whom they are dependent for the means of developing, is a delusion, and the sooner it is abandoned the better will be the opportunity for obtaining legislation based upon business principles and business experience. The investor must know in advance the conditions under which he is to conduct his business, and Federal water power laws should specifically define the terms and conditions under which permits for use of Government property necessary to the development of water powers shall be issued. This is just as necessary to the guidance of ever changing heads of Government bureaus in conducting the affairs of their departments as it is to those who would invest their money in the development of our water powers.

To be of effect, Federal legislation governing water power development must be of a nature to protect the public interest,

be fair and businesslike toward capital, and place not a feather-weight more burden on the operation of water powers subject to the control of the Federal Government than is borne by competing hydro-electric developments not subject to Federal control. There is no reason why these things should not be so co-ordinated upon a solid business basis as to protect every interest and bring results.

Thus it is apparent that there is vital and imperatively urgent necessity for the enactment of practical Federal water power legislation of a character which will promote and encourage in every way the development and utilization of the enormous quantity of energy latent in our streams and now wasting to the sea; a necessity in no way local, but national. It is necessary for the manufacture of ammunition for the national defense; necessary for the manufacture of fertilizers that the cost of living may be decreased through increase of crops; necessary for the electrification of railroads for the cheap carrying of freight, and to provide a means of rapid and comfortable transportation for the people; necessary to the irrigation of vast tracts of lands, meaning the building of thousands of homes on lands now silent; necessary to the establishment of great and entirely new industries in the United States, meaning the investment of hundreds of millions of dollars, the building of new cities and towns, and the employment of thousands of men and women; necessary if we are to maintain our commercial standing among the manufacturing nations of the earth; necessary in order that coal and oil may be preserved for the use of future generations; and finally, of vital necessity toward promoting the safety, the comfort, the welfare and the prosperity of every citizen of the United States.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

THE RELATION BETWEEN CONTACT POTENTIALS AND ELECTROCHEMICAL ACTION

By Irving Langmuir.

The history of electrochemistry has been marked by a conflict, extending over more than a century, between two theories of electrochemical action.

Volta, in 1797, showed that plates of two different metals when placed together and then separated, acquire electric charges. Thus, if copper and zinc plates are used, the copper becomes negatively while the zinc becomes positively charged.

This fundamental experiment became the basis of Volta's contact theory of electrical action. Volta found that the various metals could be arranged in a series each of which was positive with respect to those preceding it and negative to those following it. He realized that in any closed circuit consisting entirely of metallic conductors the electromotive forces would balance so that no current would be obtained. If, however, two metals in contact were connected through an electrolyte, current was observed to flow through the circuit. Volta considered that the electrolyte allowed the contact-electromotive force of the metallic junction to become effective. Naturally enough, at that time Volta did not have clear conceptions of the energy relations involved and many of his statements imply a violation of the conservation of energy.

A few years later (1800) Ritter observed that the action of the voltaic pile was always accompanied by a chemical change in the electrolyte or the electrodes. He soon drew the conclusion that the chemical change should be looked upon as the cause of the electric phenomena.

Thus two apparently opposing theories, the contact theory and the chemical theory of electromotive force, grew side by side from the early days of electrochemistry. An excellent account of the resulting conflict is given in Ostwald's *"Elektrochemie, Ihre*

Geschichte und Lehre," Leipzig, 1896. In discussing Volta's ideas as to contact electromotive force, Ostwald says (page 65): "Wir stehen hier an einem Punkte (1797) wo der folgenreichste Irrthum der Elektrochemie beginnt, dessen Bekämpfung weiterhin fast den grössten Theil der wissenschaftlichen Arbeit auf diesem Gebiet in Auspruch genommen hat."

Volta, and most of the early adherents of the contact theory, maintained that chemical changes brought about by the electric current were purely secondary. They considered that the potential differences at the contact between the two metals formed the greater part of the observed electromotive force of the cell. Volta admitted, however, that smaller differences of potential also occurred at the junction of the metals with the electrolyte.

The adherents of the chemical theory looked upon chemical action as the cause of the flow of current, but at first did not question the reality of Volta's contact potential differences. The height of the conflict between the two theories was reached in 1830, when de la Rive denied the very existence of the contact electromotive force, and even attributed the results of Volta's fundamental experiments to chemical reactions at the junction of the metal plates with the air.

The contact theory was ably defended by Pfaff and Sir Humphrey Davy. The work of Faraday (1840), however, very greatly strengthened the chemical theory. Favre, in 1866, applied the principle of the conservation of energy and showed that the electrical energy of a cell was derived from the chemical energy of the reaction. The phenomena at the contact of the metals thus gradually assumed less importance and more attention was given to the chemical changes at the electrodes. Still, the reality of contact electromotive forces of fairly large magnitude was not usually doubted.

The final overthrow of the contact theory, according to Ostwald, was brought about by Le Roux's (1866) and Edlund's (1870) studies of the Peltier effect. Peltier found in 1834 that when a current passes through the junction between two metals, heat is liberated or absorbed according as the current flows in one

direction or the other. Le Roux advanced the following theorem: "If, in a circuit, an absorption or evolution of heat occurs which is proportional to the current and changes sign with the direction of the current, then these effects correspond to and are proportional to electromotive forces of the same or opposite sign, located at those places at which the absorption or evolution of heat takes place."

Thus Le Roux calculated the contact potential between two metals by dividing the heat energy (watts) absorbed or liberated, by the current causing the effect. In this way he obtained values for contact electromotive forces which were of the order of a few thousandths of a volt. The values were one-hundredth of those found by Volta, and seemed to bear no simple relation to these.

Le Roux's work attracted very little attention, so that a few years later Edlund (1870), and later Maxwell (1873), arrived at the same conclusions independently. Maxwell stated that the Peltier effect afforded the only reliable method of determining the contact electromotive force between metals.

According to Ostwald, this evidence that the contact electromotive force between metals is entirely negligible seems to have been very generally regarded as convincing. Helmholtz and Lord Kelvin, however, maintained up to their deaths that the Peltier effect does not correspond directly to the contact potential,[1] but is related to the *temperature coefficient* of the contact potential by the following equation:

$$V_P = T \frac{dV_c}{dT}$$

where V_c is the contact potential between two metals at the temperature T and V_P is the Peltier electromotive force; that is, the electromotive force which is equivalent to the observed absorption or evolution of heat at the junction.

Lord Kelvin,[2] who contributed perhaps more to the study of the Volta effect than any other observer, was of the opinion that

[1] I cannot find that Ostwald mentions this theory of Helmholtz and Kelvin.

[2] A good statement of Kelvin's position is given in an article in the Phil. Mag. (1898), **46**, 82.

the effect was due to the attraction of the two metals for each other at their junction.

Sir Oliver Lodge (Phil. Mag. (1900) **49**, 351, 454) took the opposing side and attributed the contact potentials to the action of oxygen at the surfaces of the metal.

As a general rule, since Ostwald's and Nernst's work (1889-1893) on the potentials of electrolytic cells, electrochemists have denied the very existence of contact potentials as an intrinsic property of metals, whereas physicists have been divided in their opinions.

Whethem discusses, in a non-committal manner, the relation between "Contact Electricity and Polarization," in an excellent chapter in his book on "The Theory of Solutions," Cambridge, 1902.

Fournier d'Albe, in his book on the "Electron Theory" (1907), favors Helmholtz's view that both the contact potentials and the electrochemical potentials are measures of the attractions of the metals for electrons. He traces a similar relation between these effects and the photo-electric effect. In describing the mechanism of electrolysis, however, he looks upon Nernst's solution tension as being responsible for the action at the electrodes, and overlooks the contact potentials.

Fleming (Encyl. Brit. (1910) **9**, 183) says that "even at the present time opinions of physicists can hardly be said to be in entire accordance as to the source of the electromotive force in a voltaic couple or pile."

With the discovery of radioactivity a new and convenient method of measuring the Volta effect had been obtained. By ionizing the air between electrodes of different metals, the electric field in the air could be destroyed and the electromotive force between the metals could be measured by an ordinary electrometer without the necessity of changing the distance between the plates. The differences of potential obtained in this way were substantially the same as those found by Volta's method.

Greinacher in 1905 (Ann. Phys. (1905) **16**, 708) made a thorough investigation of the contact potentials between metals by the new method, and reached the conclusion that the effect

was caused by the presence of an adsorbed film of water which he supposed was present on all metals, even in the highest vacuum. Greinacher's work is often quoted, especially by German writers, to prove that the Volta effect is due to secondary electrolytic action and is not an inherent property of metals. (For example, Kruger, Phys. Zeitschr. (1911) **12**, 360.)

The reasons that have led to the abandonment of the contact theory of electromotive forces by electrochemists may be divided into the following three groups:

I. Energy Relations.—The electrical *energy* generated by a cell is unquestionably derived from the energy of chemical reactions taking place at the surface of the electrodes. It therefore seems probable that the *electromotive force* producing the flow of current also originates at the surface of the electrodes.

II. Irregularities in the Volta Effect.—All experimenters have found that the Volta effect is extremely sensitive to slight changes in the surface conditions. The effect could often even be reversed in sign by changing the gas between the plates. After polishing the plates the potential differences would undergo rapid changes, continuing often for long periods of time. Therefore the values obtained by different investigators sometimes differed considerably from each other and it seemed impossible to determine which values, if any, corresponded to the pure metal surface. From this work it became certain that the electromotive forces at the surfaces of the electrodes could not be neglected. On the contrary, in view of the difficulties in determining the contact potentials, it seemed more probable that the latter could be neglected in comparison with the surface potentials.

III. The Peltier Effect.—The theories and experiments of Le Roux, Edlund and Maxwell convinced most physicists and practically all electrochemists that the real contact potentials were extremely small—of the order of a few thousandths of a volt—and were therefore negligible in electrochemical problems.

Thus the long-standing conflict between the two theories was apparently finally brought to a close by the complete victory of the chemical theory.

Within the last four or five years, however, some remarkable progress has been made in certain branches of physics, which has

resulted in bringing to life again the contact potential theory. As usually happens in such cases, the new evidence in favor of the theory comes from quite other fields of science. As far as I am aware, the bearing and significance of this new work on electrochemistry has not yet been pointed out.

The recent work in physics to which I refer furnishes six distinct lines of evidence as to the reality of the contact potentials:

I. Electron emission from heated metals.

II. Thermal effects accompanying the electron emission.

III. Photo-electric effect from metals.

IV. Measurements of contact potentials.

V. Ionizing potentials of metal vapors.

VI. Single line spectra of metal vapors.

In discussing these I will group them into three pairs.

I & II. Electron Emission from Heated Metals, and Thermal Effects.

It has been known for nearly two hundred years that air in the neighborhood of incandescent metals is a conductor of electricity. Elster and Geitel studied this phenomenon in great detail and published the results of their investigations in a series of papers in Wiedemann's Annalen during the years 1882-1889.

In most of their experiments they placed a metal plate close to a metallic filament within a glass bulb, and studied the charge acquired by the plate under various conditions of filament temperature and gas pressure. They found in most gases that the filament tended to give off positive electricity when it was at a red heat, but at very high temperatures it gave off negative electricity more easily than positive. When the vessel was exhausted as completely as was possible in those days, the tendency to give off positive electricity was much decreased and did not persist, whereas the tendency to emit negative electricity was apparently stronger than ever.

A similar discharge of negative electricity from the carbon filament of an incandescent lamp to an auxiliary electrode placed within the bulb was observed and studied by Edison and has since been known as the Edison effect. Fleming, in 1896 (Proc. Roy. Soc. (1890) **47**, 118, and Phil. Mag. (1896) **42**, 52) investigated and described this effect in detail.

J. J. Thomson (Phil. Mag. (1899) **48**, 547) showed that in the case of a carbon filament in hydrogen at very low pressures, the negative electricity is given off by the filament in the form of free electrons having a mass about 1/1800 of the mass of a hydrogen atom, and constituting in reality atoms of electricity. Owen (Phil. Mag. (1904) **8**, 230) showed that a heated Nernst filament also gives off electrons and Wehnelt (Ann. Phys. (1904) **14**, 425) proved that the electric current from a lime-covered platinum cathode (Wehnelt cathode) is carried in the same manner.

Richardson (Proc. Camb. Phil. Soc. (1902) **11**, 286; Proc. Roy. Soc. (1903) **71**, 415; Phil. Trans. (1903) **201**, 516) applied the electron theory of metallic conduction to the electron emission from heated metals, and was thus able to develop a theory of this effect. In order to account for the conduction of heat and electricity by metals, Riecke and Drude had assumed that metals contain electrons which are free to move under the influence of an electric force and which are in constant vibratory motion similar to that of the molecules of a gas. Richardson assumed that these free electrons are ordinarily held within the metal by an electric force at the surface, just as the molecules of a liquid are prevented from escaping by a surface force related to the surface tension. If the velocity of an electron is sufficiently high, it may be able to overcome the surface force and escape. Since the average velocity of the vibratory motion increases with the temperature, the number of electrons which reach the necessary critical velocity to escape will increase very rapidly with the temperature. These considerations are analogous to those of the evaporation of a liquid, so that the number of electrons escaping should increase with the temperature according to the same laws as those governing the increase of the vapor pressure of a liquid as the temperature is raised.

The distribution of velocities among the electrons given off by a heated metal is given by Maxwell's law.[3]

$$dN = \frac{N}{\sqrt{\pi}} e^{-x^2} dx \qquad (1)$$

Here N represents the number of electrons in each cc. of the metal, dN is the number per cc. which have velocity components

[3] Richardson, Phil. Mag. (1908) [6] **16**, 890, and (1909) [6] **18**, 681.

in a given direction lying between v and $v + dv$. The variable x is proportional to v and is equal to

$$x = \sqrt{\frac{3}{2}} \cdot \frac{v}{\overline{v}} \qquad (2)$$

where $\overline{v}$ is the square root of the mean square velocity of the electrons and, according to the kinetic theory, may be calculated by the equation

$$\overline{v} = \sqrt{\frac{3RT}{M}} \qquad (3)$$

Here R is the gas constant 83.15 x 10^6 erg/deg., T is the absolute temperature of the metal, and M is the "atomic weight" of the electrons, namely, 0.000546 (oxygen = 16).

Substituting (3) in (2) and squaring, we obtain

$$x^2 = \frac{\frac{1}{2} Mv^2}{RT} \qquad (4)$$

Richardson assumes a force at the surface tending to hold the electrons within the metal. In order to escape, an electron must work against this force. Let the work done when a "gram molecule" of electrons (*i. e.* 6.06 x 10^{23} electrons or 96500 coulombs) escape be represented by w. The work done in escaping must be derived from the kinetic energy of the electrons, and thus only those electrons can escape which have a kinetic energy greater than the work to be done. If we let v_0 be the *smallest* velocity component perpendicular to the surface which will enable the electron to escape, then we readily see that

$$\frac{1}{2} Mv_0^2 = w \qquad (5)$$

The number of electrons dn with velocity components between v and $v + dv$ which reach a square cm. of the surface per second can be obtained by multiplying the number per cc. having this velocity by the velocity component. That is, from (1) and (4)

$$dn = vdN = N \sqrt{\frac{2RT}{\pi M}}\ x\ e^{-x^2} dx \qquad (6)$$

The total number of electrons which reach the surface with a velocity perpendicular to it exceeding v_0 is therefore

$$n = N\sqrt{\frac{2RT}{\pi M}}\int_{x_0}^{\infty} e^{-x^2}\, x\, dx = N\sqrt{\frac{RT}{2\pi M}}\, e^{-x_0^2} \tag{7}$$

where x_0 is given by

$$x_0^2 = \frac{\frac{1}{2} M v_0^2}{RT} \tag{8}$$

Combining (7), (8) and (5), we finally obtain

$$n = N\sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{w}{RT}} \tag{9}$$

I expect to show that this equation is of fundamental importance, not only in the case of electron emission from metals, but in the kinetics of nearly all electrochemical processes.

According to the theory outlined above, the emission of electrons from a heated metal, which is called by Richardson thermionic emission, is an intrinsic property of the metal and is not caused by secondary chemical reactions, nor is it dependent on or influenced by an electrostatic field around the metal. If, however, there is a negative field outside the metal surface, most of the electrons which escape will return to the metal. If a positive field is *maintained* by bringing an electrode (anode) charged to a sufficiently high positive potential close to the metal surface (cathode), then none of the escaping electrons will return to the cathode. The current which flows under these conditions cannot be increased by increasing the potential on the anode and is therefore called the *saturation current.*

The saturation current, which we may represent by i, is evidently proportional to n and is given by equation (9).

If we assume that N and w are independent of temperature, then equation (9) assumes the form

$$i = a\sqrt{T}\, e^{-\frac{b}{T}} \tag{10}$$

where a and b are constants. This equation is generally known as Richardson's equation.

Richardson, in 1902, determined the relation between the saturation current from a heated platinum wire and a cylinder around it, and found that i varied with the temperature in accordance with the equation given above. He also found the relation to hold for carbon and sodium.

Richardson has published a large number of other papers[4] on this subject in which he has given experimental and theoretical evidence that the thermionic emission from heated metals is an intrinsic property of pure metals.

Richardson's views, however, have not been very well received, and until about 1913 there was an increasing skepticism as to the reality of the effect with pure metals in the absence of gas, most observers holding that chemical reactions of some mysterious nature were responsible for the electron emission. A similar feeling, which we shall discuss under the proper heading, was manifest in regard to the photo-electric effect in the absence of gas. The investigations which were primarily responsible for this skepticism were those of Wilson, Soddy, Just and Haber, Fredenhagen, Pring and Parker.

H. A. Wilson (Phil. Trans. (1903) **202**, 243) found that the electron emission from platinum at high temperature was decreased to 1/250,000 of its former value by a preliminary heating of the platinum in oxygen or by boiling in nitric acid. The admission of a little hydrogen brought the current back to its former value.

Wilson, like nearly all his successors, took it for granted that the *smallest* value observed for the electron emission was the value characteristics of the best vacuum conditions. He therefore concluded that the electron emission from a pure platinum surface was extremely small if it existed at all.

Soddy (Phys. Zeit. (1908) **9**, 8) found that the large currents obtainable from a Wehnelt cathode stopped suddenly if the residual gases in the vacuum tube were absorbed by vaporizing some metallic calcium. This work of Soddy attracted considerable attention and made many investigators feel that thermionic currents in general were dependent on the presence of gas.

Just and Haber (Ann. Phys. (1911) **36**, 308) showed that an

[4] Phil. Mag. (1908) [6] **16**, 357; (1909) **17**, 813; (1909) **18**, 695; (1912) **23**, 594; (1912) **24**, 737; (1913) **26**, 345; Trans. Amer. Electrochem. Soc. (1912) **21**, 69, and Proc. Roy. Soc. (1914) **90**, 174.

extremely small[5] electron emission could be obtained in the dark from the alkali metals when these were acted on by chemically active gases, such as chlorine, at very low pressures. Many German investigators at once concluded that all electron emission from metals, even in high vacuum, could be accounted for by chemical reactions between the metal and the minute traces of residual gases. Fredenhagen (Phys. Zeitschr. (1914) **15**, 19) even considered that Richardson's results with tungsten in very high vacuum (in 1913) were due to "regenerative" chemical reactions.

Fredenhagen (Verh. deut. phys. Ges. (1912) **14**, 384) in 1912 studied the electron emission from sodium and potassium, two metals that Richardson had found particularly good sources of electrons, and concluded that the electrons are only emitted as a result of the presence of gas. He suggested that if a perfectly clean metallic surface could be obtained in a perfect vacuum the electron emission would cease entirely.

Pring and Parker (Phil. Mag. (1912) **23**, 192) in the same year measured the currents from incandescent carbon rods in a vacuum. They found that with progressive purification of the carbon and improvement in the vacuum the currents decreased to extremely small values. They concluded that "the large currents hitherto obtained with heated carbon cannot be ascribed to the emission of electrons from carbon itself, but that they are probably due to some reaction at high temperatures between the carbon, or contained impurities, and the surrounding gases, which involves the emission of electrons."

More recently Pring (Proc. Roy. Soc. (1913) **A 89**, 344)) repeated these experiments under still better vacuum conditions and found the former results confirmed. He concludes that "the thermal ionization ordinarily observed with carbon is to be attributed to chemical reaction between the carbon and the surrounding gas." "The small residual currents which are observed in high vacua after prolonged heating are not greater than would

[5] Less than 1 percent of the electrochemical equivalent of the gas which reacted.

be anticipated when taking into account the great difficulty of removing the last traces of gas."

Besides these reasons for doubting the existence of electron emission from clean metallic surfaces, there were other reasons which were related to the disbelief in contact potentials. Debye and Richardson, as we shall see, found a relation between w, the work done when electrons escape, and the contact potentials between metals. Thus the same reasons which had indicated that contact potentials were of chemical origin would show that electron emission must be of similar origin.

Several years ago a very thorough study of the whole question of electron emission from metals was begun in this laboratory and has continued up to the present. This work, only a small part of which has as yet been published, has convinced me that the electron emission from perfectly clean metallic surfaces in the highest vacuum is a definite property of pure metals. In the course of this work perfectly satisfactory explanations have been found for each of the causes which have led other investigators to the opposite conclusions.

The following brief review of this work will help to confirm these statements.[6]

The presence of minute pressures of oxygen or water-vapor, even as low as 10^{-9} mm. of mercury, *decreases* the electron emission from tungsten very materially. Carbon monoxide and dioxide and methane decrease the electron emission only slightly. Nitrogen has no effect except when the voltage is such as to cause ionization, and then the effect is to *decrease* the current. Hydrogen, mercury vapor and the inert gases, when pure, have no effect on the electron emission.

[6] The papers which have been published from this laboratory on the subject of electron emission are:

1. "Effect of Space Charge and Residual Gases on Thermionic Currents in High Vacuum." I. Langmuir, Phys. Rev. (1913) **2**, 402, 450.
2. "A Powerful Roentgen Ray Tube with a Pure Electron Discharge." W. D. Coolidge, Phys. Rev. (1913) **2**, 410.
3. "Effect of Space Charge." I. Langmuir, Physik. Zeitsch. (1914) **15**, 348.
4. "Electron Emission from Tungsten and the Effect of Residual Gases." I. Langmuir, Physik, Zeitsch. (1914) **15**, 516. This paper contains much data not given in the article in the Phys. Rev. (Paper 1).
5. "Determination of e/m from Measurements of Thermionic Current." S. Dushman, Phys. Rev. (1914) **4**, 121 and Physik. Zeitsch. (1914) **15**, 681.
6. "A New Device for Rectifying High Tension Alternating Currents: The Kenotron." S. Dushman, General Electric Rev., Mar., 1915.
7. "The Pure Electron Discharge and its Applications in Radio Telegraphy and Telephony." I. Langmuir, Trans. Amer. Inst. Radio Eng., Sept., 1915, and General Electric Rev., May, 1915.

As the vacuum is improved the emission in general increases, but reaches a definite limit which is not changed by further improvement in the vacuum.

In all of this work no evidence has been found that chemical reactions ever produce currents comparable in magnitude with those obtained by electron emission in high vacuum. In fact, the gases which react most vigorously with tungsten are the ones which have the greatest effect in *decreasing* the electron emission.

The effects produced by adsorbed films have been studied in detail, and these films can be produced or destroyed at will. Traces of thorium, in a tungsten filament, under certain conditions, lead to the formation of an adsorbed film of thorium metal consisting of a layer one atom deep, which increases the electron emission 10,000 fold or more. This film, however, can be distilled off by heating the filament to 2700°, and the emission thereafter corresponds to that of pure tungsten.

The electron emission from tungsten has been carefully measured over a wide range of accurately determined temperatures and the results can be expressed within the experimental error by Richardson's equation, if a is taken to be 23.6×10^6 amperes per sq. cm. and b is taken to be 52500. This corresponds to an electron emission of 0.0042 ampere per sq. cm. at 2000° Kelvin (absolute).

In these experiments the pressure was known to be *less* than 10^{-7} mm. of mercury. At this pressure the number of molecules of gas (molecular weight assumed = 30) which strike a square cm. of surface per second is[7] 3.7×10^{13}. If each of these molecules liberates one electron,[8] then the total electron emission would be 5.9×10^{-6} amperes per sq. cm. Actually, however, currents as large as 0.5 ampere per sq. cm. were readily obtained. Chemical reactions caused by residual gases thus cannot be the cause of these currents.

The electron emission from several other metals in high vacuum has been studied by the same method as that used for tungsten, and the results obtained are given in Table I, tungsten being given for comparison. Only a few experiments with each of these metals have been made, and the same care as with tungsten

[7] See Langmuir, J. Amer. Chem. Soc. (1915) **37**, 1145.

[8] Haber and Just (*l. c.*) had never observed more than one electron for each hundred molecules.

has not always been taken in studying and eliminating effects due to residual gases or impurities. The results are therefore probably much less accurate than those given for tungsten. In the table i_{2000} represents the saturation current per sq. cm. at 2000° K.

In the last column under ϕ, the work done when electrons escape from the metal is given in terms of the equivalent potential difference expressed in volts. This quantity is obtained from b as follows. By comparing equations (9) and (10) we see that

$$w = b\ R \tag{11}$$

But w is the work done when a "gram molecule" of electrons (namely, the "Faraday constant" $F = 96500$ coulombs) escape. This must be equal to $\phi\ F$ where ϕ is an imaginary potential difference occurring at the surface, equivalent in its effect to the forces which hold the electrons in the metal.[9] Therefore we may calculate ϕ from b by the equation ($R = 8.315$ watt seconds per degree):

$$\phi = \frac{w}{F} = \frac{Rb}{F} = 8.62 \times 10^{-5}\ b \text{ (volts)} \tag{12}$$

TABLE I.

Metal	a (amps./sq. cm.)	b	i_{2000} (amps./sq.cm.)	ϕ (volts)
Tungsten	2.36×10^7	52500	0.0042	4.52
Thorium	2.0×10^8	39000	30.	3.36
Tantalum	1.12×10^7	50000	0.007	4.31
Molybdenum	2.1×10^7	50000	0.013	4.31
Carbon (untreated)	.....	48000	.....	4.14
Titanium[10]	1300. ?	28000?	0.048?	2.4 ?
Iron[10]	2400. ?	37000?	0.0010?	3.2 ?

[10] Preliminary measurements made by Dr. Dushman in this laboratory.

In addition to these metals some others have been studied qualitatively. It has been found that the electron emission from pure potassium in a high vacuum is very large, even at temperatures in the neighborhood of 300-400° C. Richardson's original results with the alkali metals are therefore probably more nearly correct than the results obtained by Fredenhagen. Quantitative de-

[9] The reason for calling this potential "imaginary" will be discussed later.

terminations of the emission from these metals are in progress. Preliminary measurements with metallic calcium indicate that the electron emission is extremely high, although not as high as that from the alkali metals.

The principal reason that other observers have obtained very small currents from heated metals in high vacuum is that they failed to realize that the voltage needed to produce saturation of the current increases very rapidly when a high vacuum is reached. Lilienfeld[12] pointed this out in connection with Soddy's experiments with the Wehnelt cathode, and suggested that the effect might be caused by the building up of a negative charge in the vacuum. Lilienfeld did not give adequate reasons in support of his views and they were therefore disregarded. This effect of space charge has been studied quantitatively and in great detail in this laboratory, and we have found that it offers a complete explanation of most of the failures to obtain electron emission in high vacuum.

A number of papers have recently been published by Schottky[13] on the electron emission from metals in high vacuum. He treats several phases of the space charge problem, and gives additional experimental and theoretical evidence that the electron emission is a characteristic and fundamental property of pure metals.

The electron emission from platinum under rather bad vacuum conditions has been measured by Schlichter (Elster and Geitel Festschrift, 1915, p. 689). He obtains $a = 1.25 \times 10^7$; $b = 51060$, and $i_{2000} = 0.0035$.

The skepticism in regard to the existence of electron emission independently of chemical action has now largely disappeared. Perhaps one of the most important factors in bringing about this change of opinion is the wide-spread use of the Coolidge Roentgen Ray Tube. Any one who works long with a tube of this kind is soon convinced that its action does not depend on the chemical action of residual gases.

From the evidence which has thus accumulated in the last few years, two of the deductions from Richardson's theory may be regarded as demonstrated. These are:

[12]

[13] Phys. Zeitsch. (1914) **15**, 526, 624, 656.
Ver. deut. physik. Ges. (1914) **16**, 482.
Ann. Physik. (1914) **44**, 1011.

a. The electron emission from metals is an intrinsic property of pure metals.

b. The emission increases with the temperature according to Richardson's equation, (10).

These alone would not conclusively prove that the mechanism postulated by Richardson is the correct one. Richardson, himself, with many collaborators, has, however, shown that several other deductions from his theory are valid, namely:

c. When electrons are emitted from incandescent metals there is an absorption of energy (heat) corresponding to w, the work done when electrons escape. (Richardson and Cooke, Phil. Mag. (1913) **25**, 624; **26**, 472).

d. When electrons are absorbed (at the anode) by a cold metal, there is a liberation of heat corresponding to the value of w for the cold metal.[14]

e. The velocities of the electrons which escape from heated metals are in agreement with Maxwell's distribution law, as they should be according to Richardson's theory. (Richardson, Phil. Mag. (1908) **16**, 890; (1909) **18**, 681).

By measurements of the heat evolved by the absorption of electrons, Richardson and Cooke found $\phi = 5.5$ volts for platinum which had been saturated with oxygen by electrolysis, and $\phi = 4.5$ volts for platinum similarly saturated with hydrogen. These results agree well with values found from the electron emission from platinum. We have seen (Table I) that ϕ for pure platinum in high vacuum obtained from b of equation (10) is 4 volts. Richardson had previously found $\phi = 4.26$ volts for platinum. Wilson (Phil. Trans. (1903) **A. 202**, 243) had obtained $\phi = 5.6$ for platinum which had been boiled in concentrated nitric acid. From Deininger's (Ann. Phys. (1908) **25**, 304) results obtained under similar conditions, Richardson recalculates $\phi = 5.26$ volts.

From the heat absorption accompanying electron emission similar results have been obtained. Richardson and Cooke found $\phi = 4.7$ volts for osmium and a value of 4.24 volts for tungsten, which latter agrees fairly well with that given in Table I.

The proof that these three independent methods all give substantially the same values for w or ϕ is strong evidence of the

[14] Richardson and Cooke, Phil. Mag. (1910) **20**, 173; (1911) **21**, 404.

correctness of the fundamental assumptions upon which Richardson's theory is based.

III & IV. Photo-electric Effect and Contact Potentials.

Hallwachs, in 1888, made the important discovery that a body carrying a negative charge of electricity rapidly loses that charge when ultra-violet light falls upon it. This phenomenon, which is now generally called the photo-electric effect, is due to the action of light in causing the emission of electrons from the metal. These electrons, unlike those emitted from heated metals, have velocities independent of the temperature of the metal, but dependent in a remarkable manner on the wave length of the light used to excite them. In order to get any emission of electrons, it is necessary to use light having a wave length shorter than a definite limiting value λ_0 characteristic of the metal. This "long-wave limit" occurs in the visible spectrum in the case of the electro-positive metals, such as the alkali metals, while for a metal like platinum the limit λ_0 is at a wave length 0.28 μ (visible spectrum 0.38-0.75 μ).

The relation between the maximum velocity with which electrons are expelled and the frequency of the incident light has been the subject of some of the most important and interesting of recent physical investigations.

Einstein (Ann. Phys. (1905) **17**, 132; (1906) **20**, 199) suggested that light travels out into space in the form of bundles or quanta of electro-magnetic wave energy, and that these are absorbed as units by the atoms of matter upon which they fall. In accordance with Planck's theory of radiation the energy in these quanta was assumed equal to $h\nu$, where ν is the frequency of the light and h is the Planck constant 6.58×10^{-27} erg-seconds. According to Einstein, when a quanta of light is absorbed by an atom of a metal, its energy is imparted to one of the electrons in the atom. If the energy is sufficiently great the electron may be able to escape. In this way Einstein obtained the equation

$$\tfrac{1}{2}\, m\, v^2 = h\nu - P \qquad (13)$$

where $h\nu$ is the energy of a quanta, P is the work which must be done by the electron in overcoming surface forces, and $\frac{1}{2}\, m\, v^2$ is the *maximum* kinetic energy which the electron may retain after its escape.

Although this equation, as we shall see, has recently received the most striking confirmation, the physical hypothesis on which it was based has been entirely abandoned, even by its originator.

In 1912, Richardson (Phil. Mag. (1912) **23**, 615; **24**, 570), by means of a modified form of Planck's equation, was able to derive an equation of a form similar to (13) without making use of the hypothesis that free radiant energy exists in the form of "light quanta." Richardson also showed that the work function P, of Einstein's equation, should be identical with the quantity w which occurs in Richardson's theory of electron emission from heated metals. Furthermore, Richardson showed a relation between the velocity of photo-electrons and the *contact potentials* between metals. The theory of the relation between the three effects, electron emission by heat, contact potential and photo-electric effect, is briefly as follows:[15]

Let us consider a vacuous enclosure divided into two parts A and B by a surface S. We assume that A and B contain electron atmospheres in thermal equilibrium and that a force exists at the surface S which tends to prevent electrons from passing from A into B. Let w be the work per "gram molecule" (96500 coulombs) which the electrons have to do in order to pass through the surface from A to B. Let N_A and N_B be the concentration of electrons in A and B respectively. Then by equation (9) the number of electrons which passes (per sq. cm.) from A into B will be

$$n_A = N_A \sqrt{\frac{RT}{2\pi M}}\, e^{-\frac{w}{RT}} \tag{14}$$

The number of electrons per sq. cm. n_B which passes from B to A will be the same as if w were zero; that is:

$$n_B = N_B \sqrt{\frac{RT}{2\pi M}} \tag{15}$$

In a state of equilibrium n_A and n_B must be equal, so that we may equate (14) and (15) and thus obtain

$$\frac{N_B}{N_A} = e^{-\frac{w}{RT}} \tag{16}$$

This may also be written:

$$w = RT \ln \frac{N_A}{N} \tag{17}$$

[15] Debye, Ann. Physik. (1910) **33**, 441.
Richardson, Phil. Mag. (1912) **23**, 263, 615; **24**, 570.

This equation is of very fundamental importance in the kinetic theory of gases, and has been proved to hold with a high degree of generality even under conditions where the laws of ideal gases are inapplicable. Wherever we have two systems of gas molecules or electrons in thermal equilibrium with each other, but so related that work (w) is done when the molecules pass from one system to the other, then the concentrations (or pressures) in the two systems must differ in the manner indicated in equation (16).

Let us now consider an initially uncharged metallic body placed in a vacuous enclosure maintained at a constant high temperature. According to Richardson's theory of electron emission from heated bodies, the metal will give off electrons and become positively charged. A steady state will ultimately be reached in which electrons are drawn back into the metal at the same rate at which they escape. In this equilibrium condition equation (16) will apply. Different points in the space around the metal body will be at different electrostatic potentials. If we choose two points, A and B, having the potentials V_A and V_B then the work done when 96500 coulombs of electrons pass from A to B will be $(V_A - V_B)\,F$ where F is the Faraday constant (96500 coulombs).

Substituting this in (16) we find, after taking the natural logarithm:

$$V_A - V_B = \frac{RT}{F}\, ln\, \frac{N_A}{N_B} \qquad (18)$$

It should be noted that this equation is identical with Nernst's equation for electrochemical potentials, although its method of derivation is very different.

We may now consider the case of two metallic bodies *1* and *2* placed in the same vacuous enclosure maintained at constant temperature. Let w_1 and w_2 be the work functions corresponding to the escape of electrons through the surfaces of bodies *1* and *2* respectively. Let V_1 and V_2 be the potentials in the space just outside the surfaces of the bodies *1* and *2*. The total work which must be done in removing one coulomb of electrons from the metal *1*, in carrying them from the surface of *1* to that of *2*, and in bringing them into the metal *2*, will evidently be $w_1 + (V_1 - V_2)\,F - w_2$. According to equation (17) this must

be equal to RT times the natural logarithm of the ratio of the concentrations of the electrons in the two metals. Thus we obtain:

$$V_1 - V_2 = \frac{1}{F}\left(w_2 - w_1 + RT\, ln\, \frac{N_1}{N_2}\right) \qquad (19)$$

According to this theory, when equilibrium is reached between the two metals, there will be a difference of potential $V_1 - V_2$ between their surfaces.

Suppose now we bring the two metals into actual contact at one point. It is evident that we may still apply the above reasoning to the portions of the surfaces which are not in contact. It must thus follow from energy considerations that the difference of potential between the surface of the metals must remain the same after they are brought into contact. Equation (19) therefore gives us a method of calculating the *contact potential* $V_1 - V_2$ from the values of w_1, w_2, N_1 and N_2 for the metals in question. Richardson says: "The values of the electrical conductivity and some other considerations indicate that the number n of free electrons in unit volume is of the same order of magnitude for all the metallic conductors, and the term $RT\, ln\, (N_A/N_B)$ is found to lead to comparatively small electromotive forces of the order of magnitude of those required to account for the Peltier effect." We may therefore neglect this term, so that equation (19) reduces to

$$V_1 - V_2 = \frac{w_2 - w_1}{F} \qquad (20)$$

Or if we express w in volts according to equation (12), we obtain:

$$V_1 - V_2 = \phi_2 - \phi_1 \qquad (21)$$

We are thus enabled to calculate the contact potential between two metals from data on the electron emission at high temperatures. We shall see that these theoretical results of Debye and Richardson have received striking experimental confirmation within recent years.

According to Einstein's theory of the photo-electric effect, the

action of light on a metal is to cause electrons to be ejected from atoms with a kinetic energy $h\nu$ where ν is the frequency of the light vibrations. Many of these electrons are emitted from atoms some distance below the surface, so that most of the electrons lose a large part of their energy before they reach the surface. A few, however, will reach the surface with the maximum velocity corresponding to the energy $h\nu$. In order to escape they must do an amount of work P (equation 13) against the surface forces. Richardson considers that this work is the same as that corresponding to the w obtained by the electron emission from heated metals. It is evident, according to this theory, that no electrons can escape from the metal if the value of $h\nu$ is less than P. The minimum frequency ν_0 (corresponding to maximum wave length λ_0) at which any photo-electric effect can be observed is thus determined by the equation

$$h\nu_0 = P \tag{22}$$

The work P applies to a single electron, whereas we have taken w to apply to one coulomb of electrons (containing $N = 6.062 \times 10^{23}$ electrons). We thus obtain, since $h = 6.585 \times 10^{-27}$ erg sec.,

$$w = NP = Nh\nu_0 = 0.00399\ \nu_0\ ergs \tag{23}$$

or by equation (12),

$$\phi = \frac{Nh\nu_0}{F} = 4.14 \times 10^{-15}\ \nu_0\ volts \tag{24}$$

or, since $\lambda_0\nu_0 = 3.0 \times 10^{10}$ cm./sec. = velocity of light,

$$\phi = \frac{12.41 \times 10^{-5}}{\lambda_0}\ volts \tag{25}$$

For frequencies of light higher than ν_0 (that at which the photo-electric effect begins) Einstein's equation should give the maximum energy with which electrons can escape from the surface. These maximum velocities can be measured by determining the greatest opposing potential against which the electrons can move.

Diagrammatically, the arrangement may be represented as in Fig. 1. The metal to be investigated, A, is exposed to the action

of ultra-violet light from the source L, and is placed close to a metal plate B used to catch the electrons given off by A. A potentiometer P makes it possible to impress any desired potential on the plate. An electrometer E serves to measure the small currents set up by the electrons which strike B.

Let V_A and V_B be the potentials of A and B respectively. Then the work to be done to carry an electron from just outside the surface of A to the surface of B will be $(V_A - V_B)\,e$ where e is the charge on an electron. Since this energy must be derived from the kinetic energy retained by the electron after its escape from A, it cannot exceed $h\nu - P$. Thus no electron current can flow from A to B unless the quantity $(V_A - V_B)\,e$ is less than $h\nu - P$. We may therefore measure $h\nu - P$ by finding the largest value of $V_A - V_B$ for which current will still flow.

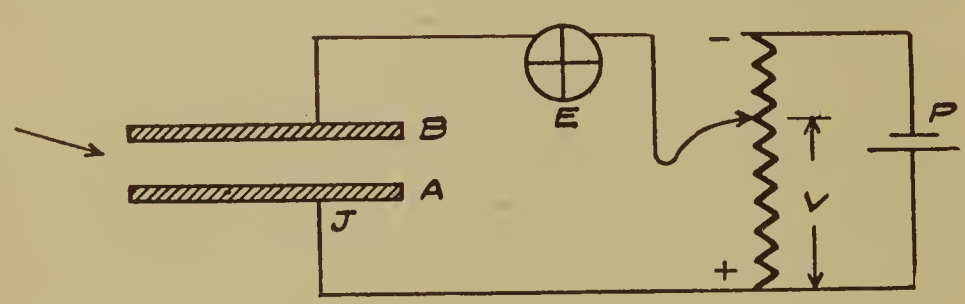


FIG. 1.

Richardson pointed out that the potential difference $V_A - V_B$ is not equal to the potential V applied by the potentiometer (shown by P, Fig. 1), but is equal to

$$V_A - V_B = V + K \tag{25, a}$$

where K is the contact difference of potential between A and B and is equal to

$$K = \phi_B - \phi_A \tag{26}$$

If we let V represent the greatest opposing potential from the electrometer which still allows current to flow, then

$$(V + K)e = h\nu - P \tag{27}$$

By multiplying this by N/F and combining with (12), it may be made to take the form

$$V + K = \frac{Nh\nu}{F} - \phi_A \tag{28}$$

The coefficient Nh/F, according to equation (24), is equal to 4.14×10^{-15} volt-seconds.

Experimentally V may be determined as a function of ν. According to equation (27), there should be a linear relation between these variables as indicated by the heavy line SU in Fig. 2. The slope of this line gives the value of Nh/F and thus serves as a very accurate means of determining h.

As the frequency of the light is decreased, the opposing potential V must also be decreased and must finally be made negative; that is, the plate B must be positively charged by the potentiometer in order to counterbalance the contact potential K. However, when the frequency is decreased to ν_0 all photo-electric effect ceases, so that the curve STU ends sharply at S.

The ordinate RS must be equal to the contact potential K.

This contact potential may, however, be readily obtained experimentally by means of the apparatus shown in Fig. 1. If the plates A and B are at different potentials, they constitute a charged condenser. If the distance between them is changed, then the capacity is altered, so that the potential difference also changes and is indicated on the electrometer E. But if the plates are brought to the same potential by the potentiometer P then no deflection occurs when they are separated. Under these conditions the potential applied by the potentiometer just balances the contact potential and serves as a measure of it.

By means of the apparatus shown in Fig. 1 the following data may be obtained in any single experiment:

1. The value of ϕ_A. This is obtained from ν_0 (abscissa of R, Fig. 2) by means of (24).

2. The contact potential K by means of the ordinate RS, Fig. 2.

3. The contact potential K by direct measurement (condenser method).

4. The value of h from the slope of the line SU.

Since $K = \phi_B - \phi_A$ the value of ϕ_A found by *1* enables us to determine ϕ_B.

The theory is thus eminently susceptible to experimental verification.

Richardson and Compton have verified several of the conclusions derived from this theory, but the work of Millikan (Proc.

Nat. Acad. Sci. (1916) **2**, 78; Phys. Rev. (1916) **7**, 355; Phys. Rev. (1914) **4**, 73), and also a paper by Hennings (Phys. Rev. (1914) **4**, 228), extending over several years, has conclusively proved that all the above deductions from Richardson's theory are accurately applicable to photo-electric phenomena.

In this work, clean fresh metallic surfaces have been obtained by cutting the metal in a very high vacuum (pressure probably about 10^{-5} mm. of mercury) and the measurements of the photo-currents and contact potentials were made immediately thereafter.

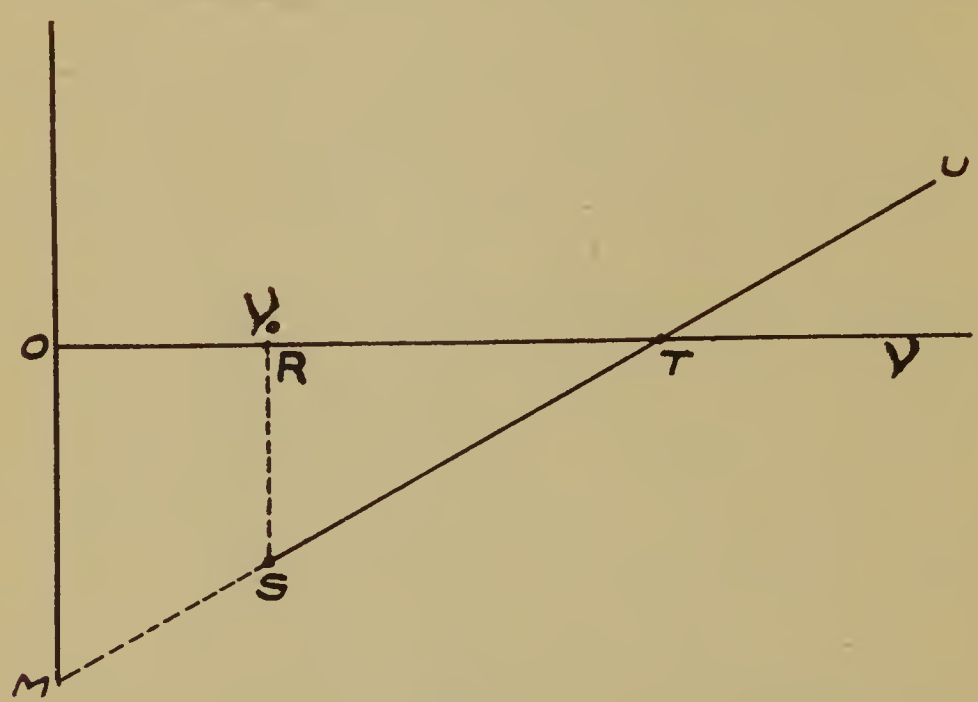


FIG. 2.

Millikan summarizes his results somewhat as follows:

1. There is a definite maximum energy of electronic emission under the stimulation of a given frequency.

2. When V is plotted against ν a straight line (STU Fig. 2) is obtained.

3. The slope of this line multiplied by F/N is 6.57×10^{-27}, a value which is in complete agreement with the best values of h determined in other ways.

4. The values of the contact potential obtained by direct measurement (method *3*) are in full accord with those obtained by the method *2* given above.

5. If ϕ_A and ϕ_B are determined separately by means of ν_0 (by illuminating first A and then B), and these values are substituted in the equation $K = \phi_A - \phi_B$, then the value of K thus

obtained is found to be in good agreement with those found by the two previously described methods.

6. Contact potentials are independent of the temperature. This is important, in that it shows that the values of ϕ found at high temperatures by means of the thermionic emission should be the same as those found at low temperatures by means of the photo-electric effect.

The three phenomena, contact potential, photo-electric effect and thermionic emission, are thus shown to be intimately related to each other. The quantity ϕ (or w) may be called the "electron affinity" of the metal, since it is a quantitative measure of the work done in separating electrons from the metal. It is this affinity which determines the behavior of the metal in each of these three effects. It is evident, therefore, that if contact potentials are to be explained as the result of chemical action, the same explanation must be used for the thermionic and photo-electric effects. We have seen that the attempt has been made to explain the thermionic effect in this way.

Similar attempts have been made in the case of the photo-electric effect. Pohl and Pringsheim (Physik. Zeit. (1913) **14**, 1112) found under certain conditions that the photo-electric effect was much decreased by improving the vacuum, and suggest that perhaps the whole effect is due to interaction between the metal and residual gases. Wiedmann and Hallwachs—the latter the discoverer of the photo-electric effect—(Verh. deut. phys. Ges. (1914) **16**, 107) go further and state emphatically as a conclusion from experiments with potassium that "the presence of gas is a necessary condition for appreciable photo-electric electron emission."

Fredenhagen and Kuster (Phys. Zeit. (1914) **15**, 65, 68) conclude that the same is true for the photo-electric effect from zinc, and in a still later publication Fredenhagen (Verh. deut. phys. Ges. (1914) **16**, 201) claims to find that both the thermionic emission and the photo-electric emission from potassium are entirely dependent on the presence of gas.

Dr. Dushman in this laboratory has repeated Hallwachs' and Fredenhagen's experiments (Physik. Zeit. (1914) **15**, 524) under much better vacuum conditions than those employed by the Ger-

man investigators, and finds no difficulty in obtaining both thermionic and photo-electric electron emission. One of the reasons for their failure to obtain emission may have been the same as in the experiments of Pring and Parker on thermionic emission, namely, disregard of the space charge phenomena and of the charging up of the walls of the apparatus.

Perhaps one of the best indications that these results of Wiedmann and Fredenhagen are due to secondary causes is that Millikan[16] by cutting fresh metal surfaces in very high vacuum, finds that the photo-electric effect still persists.

Another reason for believing that the photo-electric property is an intrinsic property of pure metals is afforded by the fact that Einstein's equation has been verified with high accuracy[17] in the case of the production of Roentgen rays by rapidly moving electrons, and also in the reverse process of the emission of high velocity electrons by Roentgen rays. There is thus the best of evidence that the maximum velocity with which electrons are set into motion by light is exactly given by the equation $\frac{1}{2}mv^2 = h \cdot \nu$ It is certain that the electron emission by Roentgen rays is not caused by chemical action, and the probability is thus great that the electron emission by light (which follows the same law) must also be the direct result of the action of the light.

Because of the relationships between the different phenomena, a proof that any one of them is not caused by chemical action must be considered to be proof that none of them is so caused.

It is, however, a fact beyond question that the presence of films on the surface of metals, such as may be produced by chemical action, may enormously alter all three of the phenomena—contact potential, thermionic effect and photo-electric effect. This may be brought about either by formation of a charged double layer (Richardson), which has the effect of changing the value of ϕ, or by covering up a portion of the surface (Langmuir) with a material which has a very different electron emission. On this theory we should therefore expect (and we actually find in practice) that the three different classes of phenomena are affected in similar ways by any of the factors which may alter the surface conditions.

[16] Loc. cit.

[17] A. W. Hull, Phys. Rev. (1916) 7, 156.

V & VI. Ionizing Potentials and Single Line Spectra.

The electron affinity ϕ of different metals should be related to many other properties of metals beside those we have considered thus far. Hughes (Phil. Mag. (1913) **25**, 683), has suggested that the ionizing potential of a metal vapor[18] may be equal to ϕ and on the basis of this assumption has endeavored to calculate the ionizing potential of oxygen from the wave length of the ultra-violet light at which oxygen begins to absorb the light strongly. The ionizing potential is a measure of the work which must be done to remove an electron from a neutral gas molecule, while ϕ is the work needed to remove an electron from the surface of a solid metal. There is no good inherent reason to think that these two quantities should be equal, but we may reasonably expect that they should run more or less parallel.

Frank and Hertz (Verh. d. deut. Phys. Ges. (1914) **11**, 512) have found the ionizing potential of mercury vapor to be 4.9 volts. Furthermore, when electrons with a velocity only slightly more than 4.9 volts were allowed to collide with mercury atoms, they observed that the mercury vapor emitted a spectrum consisting of a single line of wave length 253.7 $\mu\mu$. Frank and Hertz pointed out that the energy of an electron which has fallen through a potential difference of 4.9 volts is almost exactly equal to a quantum of energy $h\nu$ where ν is the frequency corresponding to the observed spectrum line. The voltage corresponding to any given wave length according to the quantum theory may be calculated by equation (25) which we have used in calculating the voltage corresponding to the long wave limit in the photoelectric effect. The wave length 253.7 thus corresponds to 4.89 volts, well within the experimental limit of error of Frank and Hertz's value.

McLennan and Henderson (Proc. Roy. Soc. (1915) **A**, **91**, 485; Journal Franklin Inst. (1916) **181**, 191) have shown that by using very low voltages (4-13 volts) various other metal vapors may be made to emit single-line spectra. The lines obtained in this way may also be observed as absorption lines under

[18] The ionizing potential of a gas is the difference of potential through which an electron must move in order to acquire sufficient velocity to cause ionization when it collides with a neutral gas molecule.

certain conditions. McLennan assumes that these single lines correspond to the ionizing potentials. In this manner they obtain the values given in Table II.

TABLE II.

Ionizing Potentials Calculated from Single-Line Spectra.

Element	Wave Length	Ionization Potential[19]
Mercury	253.7 μμ	4.89 volts
Zinc	307.6 "	4.04 "
Cadmium	326.0 "	3.81 "
Magnesium	285.2 "	4.35 "
Calcium	422.7 "	2.94 "
Strontium	460.8 "	2.69 "
Barium	553.6 "	2.24 "

Single-line spectra have not yet been found in the cases of the alkali metals, so that the ionizing potentials of these cannot yet be obtained in this way. It is, however, of some interest that the first lines of the principal series of these elements furnish values for the ionizing potentials which seem to be entirely reasonable and consistent with the known properties of these elements and their relations to other elements. The values so obtained are given in Table III. Whether or not these lines actually correspond to the ionizing potentials can only be determined by further experiment.

TABLE III.

Hypothetical Values of Ionizing Potentials Calculated from First Lines of the Principal Series in the Spectra of the Alkali Metals.

Element	Wave Length	Ionization Potential
Lithium	671 μμ	1.85 volts
Sodium	589 "	2.11 "
Potassium	770 "	1.61 "
Rubidium	795 "	1.56 "
Caesium	894 "	1.39 "

DISCUSSION REGARDING THE MEASUREMENT AND NATURE OF CONTACT POTENTIALS.

The evidence that has accumulated in the last few years and which has been reviewed in the preceding pages, affords conclusive proof that contact potentials exist independently of chemical reactions, and are of the same order of magnitude as those

[19] Calculated from the wave lengths by equation (25).

observed by Volta. This opinion is, however, by no means universally held and much more will need to be published on this subject before it becomes so. A large amount of unpublished data of a more or less qualitative nature has been obtained in this laboratory which very greatly strengthens our conviction that the effect is a genuine and inherent property of pure metals. Thus we have observed large contact potentials (a couple of volts) between tungsten and potassium under conditions of vacuum very much better than even those described by Millikan. Chemical reactions with the small pressures of residual gas furnish an entirely inadequate explanation of such effects. The results of a series of measurements of contact potentials on several metals with freshly prepared clean surfaces, in exceptionally good vacuum, will probably be published in the near future.

The Volta series of the elements is determined by the magnitude of ϕ, the electron affinity. As soon as it is established that this quantity is an inherent property of pure metals its significance becomes very great, and it is a matter of importance to determine it with accuracy. Unfortunately, the experimental difficulties have been so great that very few accurate determinations of this quantity are available. Although it is certain that the effects observed are not due directly to chemical action, it is equally certain that very minute traces of chemically active gases will produce surface films which alter (usually decrease) the contact potentials.

From the descriptions that have been published it is felt that none of the experimental conditions which have been employed, except some of those used in this laboratory, have been such as to give clean metallic surfaces. Millikan's experiments have undoubtedly been the best in this regard, yet even here there is very good evidence that the metal must have been oxidized before his first measurements were made. In Millikan's experiments, the glass vessel enclosing the apparatus for cutting the metal surfaces had not been heated to high temperature to drive off moisture. Now Dushman (Phys. Rev. (1915) **5**, 224) has shown in this laboratory by means of a highly sensitive vacuum gage devised by the writer (Phys. Rev. (1913) **1**, 337), that even with a Gaede molecular pump exhausting through a glass tube 3.0 centimeters internal diameter (about 5 ft. (150 cm.) long)

the pressure did not fall below 0.2 bar[20] even after exhausting continuously for one hour. By placing a liquid air trap between the pump and the gage, the pressure fell to 0.09 bar. By baking out the bulb containing the gage at 300° C. for one hour, the pressure became 0.03 bar, but to obtain still lower pressures it was necessary to heat all the tube connecting to the pump. The pressure thus fell to *less* than 0.0007 bar. The pressures that thus persist in an apparatus which has not been thoroughly baked out are due mostly to water vapor, which is given off at such low pressures that it can only be removed extremely slowly by the pump. It has previously been shown (J. Amer. Chem. Soc. (1913) **35**, 106; Trans. Amer. Inst. Elect. Eng. (1913) **32**, 1920), on heating a 40-watt lamp bulb to 200° C., that 200 cu. mm. of water vapor[21] (not shown by McLeod gage), 5 cu. mm. of carbon dioxide and 2 cu. mm. of nitrogen are given off, although the bulb had been previously dried out for 24 hours at room temperature by exposure in a good vacuum to a tube immersed in liquid air.

In Millikan's experiments the surface of glass exposed (to say nothing of the metal parts which also adsorb gas) was very much greater than that of the 40-watt bulb, probably ten times as great. It is reasonable to suppose, therefore, that the glass walls even after 24 hours' exposure to the pump retained several cubic centimeters of gas. Experience of many kinds has proved in this laboratory that this gas slowly leaks off at room temperature. Millikan estimates that the pressure in his apparatus was about 0.001 bar. One cubic cm. of gas at atmospheric pressure would have a volume of 1,000,000 *liters* at a pressure of 0.001 bar. How long would it take to exhaust this quantity of gas at this pressure?

It may be shown from a formula given by Knudsen (Ann. Phys. (1909) **28**, 76), and which has been thoroughly tested in this laboratory, that the maximum speed S at which air may be exhausted through a tube of length L and diameter D is

$$S = 12200 \frac{D^3}{L} \tag{28}$$

[20] The bar is the C. G. S. unit of pressure, and is equal to one dyne per sq. cm., or 0.00075 mm. of mercury (¾ micron). This unit of pressure is particularly convenient for all low-pressure work. It is almost exactly one-millionth of an atmosphere.

[21] These volumes are reduced to atmospheric pressures.

If D and L are expressed in cm., S represents the speed in cubic cm. per second, at the pressure of the gas in the vessel being exhausted. If in Millikan's experiments the tube connecting to the pump had an effective internal diameter of 0.8 cm. and a length of 50 cm., then $S = 125$ cc. per second is the maximum speed of exhaustion. At this rate it would take 95 days to remove the million liters of gas which correspond to one cubic centimeter at atmospheric pressure. From this we may conclude that the pressures in Millikan's experiments were always much above 0.001 bar.

On the other hand it may be shown[22] that a pressure even as low as 0.001 bar of a chemically active gas, such as water vapor, is sufficient to cause the formation of an adsorbed film of molecular thickness within about 3 seconds. We have found films of this thickness to have a very great effect on thermionic emission and may conclude that the effect on contact potentials would be equally important. Millikan's measurements were never carried out in less than 15 seconds, so there is good reason for believing that the surfaces were not pure. The absence of fatigue in his experiments may be only an indication that the formation of a film of more than molecular thickness takes place slowly.

The experiments of Hughes (Phil. Trans. (1912) **212**, 205, and Phil. Mag. (1914) **28**, 337) on the photo-electric effect and contact potentials of freshly distilled metals (in vacuum) were made under much worse vacuum conditions. In fact, various experiments in this laboratory have shown that films of metal distilled in apparatus which has not been baked out show signs of very marked contamination, even their mechanical and optical properties being seriously affected by the gases carried down with them.

It may be well to contrast with these conditions those used by

[22] This calculation is as follows: In a previous article (J. Amer. Chem. Soc. (1915) **37**, 1145, the number of gas molecules which strike a sq. cm. of a surface per second was shown to be

$$n = 2.65 \times 10^{19}\, p/\sqrt{MT}$$

where p is the pressure in bars, M is the molecular weight of the gas, and T is its temperature. For water vapor ($M = 18$) at 300° absolute and 0.001 bar pressure, this gives $n = 3.6 \times 10^{14}$ molecules per sq. cm. per second. To cover a sq. cm. with a layer one molecule deep would take about 10^{15} molecules. Thus if every molecule striking the surface should adhere to it or condense on it, it would only take 3 seconds for the surface to be practically covered. It will be shown in a paper soon to be published that there are excellent reasons for believing that nearly every molecule of an active gas reacts or condenses on a surface on its first collision with the surface. It is thus highly probable that the surface would be covered by a film of some sort within a very few seconds, even at as low a pressure as 0.001 bar.

the writer in his determination of the electron emission from tungsten at high temperatures (Physik. Zeitsch. (1914) **15**, 519). Two tungsten filaments were mounted side by side in a bulb by welding them to platinum leads which had previously been fired in a vacuum furnace to free them from gas. The bulb was exhausted by a molecular pump (using also liquid air trap) for several hours while being heated to 360° C., during which time the filaments were heated to a high temperature to drive off gas. The bulb was then sealed off and both filaments were aged at a high temperature. Previous work with a vacuum gage (Dushman *l. c.*) had proved that this treatment cleans up residual gases to a remarkable degree, so that even when the bulb is less perfectly baked out (250° C.) the pressure is lowered well below 0.001 bar. The electron emission was now measured, one filament being used as cathode and the other as anode (both electrodes gas-free). In order to still further improve the vacuum the bulb was kept completely immersed in liquid air while one of the filaments was heated until it vaporized so much that a dense deposit of tungsten collected on the bulb. The electron emission was now again determined (bulb still in liquid air) using part of the time the gas-free tungsten deposit on the bulb as anode. The vacuum must have been extraordinarily high (probably of the order of 10^{-9} bars) in this experiment, for it has been found that tungsten vapor under these conditions combines with all known gases except the inert gases, and, in addition, with the bulb at low temperatures, has a strong tendency to adsorb even the latter gases. Furthermore, it has been shown that the inert gases (which are the only ones which could withstand such treatment) have no effect on the electron emission. Notwithstanding the enormous decrease in pressure which must have been produced by this treatment, no change occurred in the electron emission, proving conclusively that the presence of gas was not essential to the phenomenon.

In order to make sure that the effect was not influenced by a very stable adsorbed film on the surface of the filament, the latter was heated in some cases to a temperature at which a perceptible thickness of tungsten was distilled from its surface. But even this treatment brought about no change.

In order to obtain absolutely trustworthy data in regard to the electron affinity of metals it will probably be necessary to resort to distillation of metals in a similarly high vacuum. Work of this character with a number of different metals is in progress.

For the present, therefore, we must remain content with approximate values of the electron affinity for most of the metals. I have endeavored to collect together the best of the available data, and present them in Table IV.

It is seen that the agreement between different observers is usually within a few tenths of a volt. In the case of magnesium Richardson's sample was probably oxidized. Henning's value for this metal was found immediately after cutting a fresh surface and he found that this metal was more affected by admitting air than any of the others which he studied.

The ionizing potentials, as determined from the spectrum, is of the same order of magnitude as ϕ, but in the case of magnesium the difference is much larger than the probable error. It seems, therefore, that the work necessary to take an electron from an atom of a metal vapor is only approximately equal to that needed to separate it from the solid metal. It is a remarkable fact that they should be as close together as the results indicate.

MECHANISM OF ELECTRON EMISSION AND CONTACT POTENTIAL.

According to the old Volta theory, the seat of the potential difference was at the junction of the two metals. According to the chemical theory, the electromotive force was located at the junction of the metals with the electrolyte, or in the case of Volta's condenser experiment the electromotive force was thought to be at the junction of the metal with the air or surrounding space.

An examination of Richardson's theory of contact potentials shows that it does not inherently involve any assumption as to the location of the potential difference. The contact electromotive force $V_1 - V_2$ (equation 19) is the difference of potential between points just outside of the surfaces of the two metals.

Helmholtz has proved that wherever there is a discontinuity of potential at a surface there must be an electric double layer, consisting of positive and negative surface charges separated by a small distance. It is possible to assume that such double layers

TABLE IV.

The Electron Affinity of the Elements

ϕ in Volts.

Method:	Contact (Henning)	Thermionic (Langmuir, Table I)	Photo-electric and Contact (Millikan.)	Photo-electric (Richardson)	Miscellaneous	Single Line Spectra Tables II or III
Tungsten	....	4.52	....	...	....	....
Platinum	....	....	....	4.3	4.45	....
Tantalum	....	4.31	....	...	....	....
Molybdenum ..	....	4.31	....	...	....	....
Carbon	....	4.14	....	...	....	....
Silver	4.05	....	....	...	....	....
Copper	(4.0)	....	....	4.1	....	....
Bismuth	....	....	....	3.7	....	....
Tin	3.78	....	....	3.5	....	....
Iron	3.86	3.2(?)	....	...	....	....
Zinc	3.46	....	....	3.4	....	4.04
Thorium	....	3.36	....	...	....	....
Aluminium	3.06	....	....	2.8	....	....
Magnesium ...	2.63	....	....	3.2	....	4.35
Titanium	....	2.4(?)	....	...	....	....
Lithium	....	....	2.35	...	....	1.85
Sodium	....	....	1.82	2.1	....	2.11

exist at the surfaces of metals and that these cause a discontinuity of potential at their surfaces. In this case it is unnecessary to assume any difference of potential at the junction between the metals. But it must not be assumed that these double layers are produced by chemical action or by gases; they must be inherent to even pure metal surfaces.

On the other hand, the existence of surface double layers on pure metals may be denied and it may be assumed that a double layer exists at the junction of the metals. Either assumption would fit in equally well with Richardson's theory and would give the same relationships between thermionic, photo-electric and contact phenomena.

The main fact brought out by the work of Richardson and his collaborators is that there exists, *in the space around two metals in contact,* an electric field which is a result of intrinsic properties of pure metals.

Although the validity of Richardson's theory is in no way affected by assumptions regarding the location of the potential discontinuity, yet there are good reasons for assuming that the contact potential is actually located at the junction of the metals.

A study of the probable mechanism of the emission of electrons will make this clearer.

Richardson* (Phil. Mag. (1912) **23**, 278) in discussing the nature of the work w, points out that if electrons were infinitely small, it would be necessary to assume a double layer at the surface in order to account for finite values of w. But with electrons of finite size there may be a difference of *potential energy* between an electron inside and outside the metal, even when no double layer is present, due to "the work done by the electron against the attraction of its image[23] in the conductor. This is not infinite, as in

[23] When a charged body is brought close to a metallic conductor, a charge of opposite sign is induced in the surface of the conductor and this exerts an attraction on the charged body. Sir Wm. Thomson has shown that in such cases the attraction is the same as if the conductor were replaced by a second charged body having the shape and position of the optical image of the first charged body reflected in the surface of the conductor. If the conductor is a plane surface, the optical image of an electron situated at a distance x outside the surface would be located at a point at a distance x behind the surface. The attraction between a positive and a negative electron separated by the distance d is e^2/d^2. Hence by Thomson's "method of images," the attraction between an electron and a metallic conductor (plane surface) would be $e^2/(2x)^2$.

* A similar theory had been previously advanced by Jentzsch (Ann. Physik. (1908) **27**, 129) and had been developed in detail by Debye (Ann. Physik. (1910) **33**, 441).

the ordinary electrostatic theory, because the volume density of the electrification in the ultimate atoms of positive and negative electricity is finite."

"This discussion brings out the necessity for using great care in the employment of the terms electric force and electric potential in problems of this character."

Electric potential must, however, be defined in a manner consistent with the application of the potential function in other branches of science.[24]

If we have two points, A and B, between which we wish to measure the difference of potential, we determine the amount of work W which must be done to move an electric charge e from A to B. In the great majority of practical cases we find that the work W is proportional to the charge e, so that we may then define the potential difference as W/e; that is, the work done to move the unit charge from A to B. In the cases that we shall now consider, however, we find that W is not proportional to e. In order to be consistent, it then becomes necessary to define the potential difference as the limiting value of W/e, when e decreases without limit. In other words, the potential difference is dW/de.

Let us now return to consider an electron escaping through a metallic surface at which no electric double layer exists. According to Helmholtz, there will be no difference of potential between the interior of the metal and the space immediately surrounding it. An infinitesimal electric charge could pass through such a surface without doing any work. But an actual electron coming from within the metal must be subjected to an attractive force the moment it gets beyond the surface layer of atoms. This force does not exist independently of the electron, but is called into existence by the mere presence of the electron. By the theory of images it is evident that the work which the electron will have to do in order to escape will be proportional to e^2, where e is the charge on the electron.

Schottky (Physik. Zeitsch. (1914) **15**, 872), in order to estimate the effect of intense electric fields on thermionic currents,

[24] Magnetic potential, gravitational potential, velocity potential, etc.

has extended this theory by making a definite hypothesis as to the manner in which the attractive force varies when the electrons are close to the surface of the metal.

The force exerted on an electron by the charge induced in a perfectly conducting plane at a distance x is

$$F = \frac{e^2}{4x^2} \tag{29}$$

The work done dw in increasing the distance by an amount dx is thus given by the equation

$$dw = \frac{e^2 dx}{4x^2} \tag{30}$$

This equation is only valid when the electron is at such a distance from the metal surface that the induced charge may spread over the surface, as postulated by the electric image theory. Obviously, for distances comparable with the dimensions of the atoms, this relation must break down. We may assume that for distances greater than x_0 the equation (29) is valid, but that some other law of force $F(x)$ holds for distances less than x_0. The total work done when an electron escapes from a metal will thus consist of two parts, as follows:

$$W_0 = \int_0^{x_0} F(x)\, dx \tag{31}$$

$$W_1 = \int_{x_0}^{\infty} \frac{e^2 dx}{4x^2} = \frac{e^2}{4x_0} \tag{32}$$

$$W = W_0 + W_1 \tag{33}$$

The manner in which the attractive force between the electron and the surface may be assumed to vary is illustrated in Fig. 3. The ordinates represent the force acting on the electron when it is at a distance x from the surface. The curve SPT gives the law of force represented by (29), which is only valid to the right of the point P ($x = x_0$). For values of x less than x_0 we may make various assumptions as to the law of force.

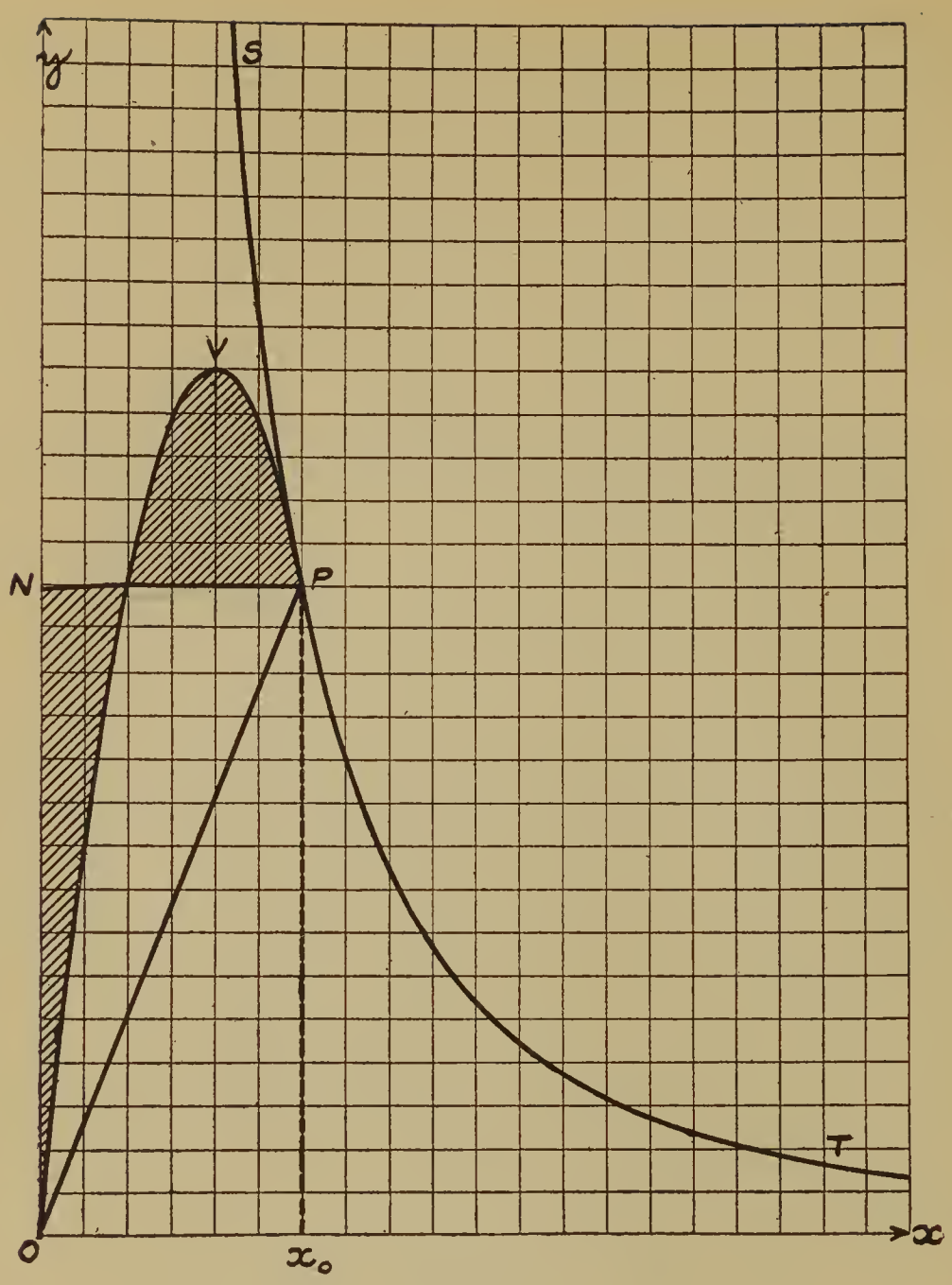


FIG. 3.

1. Schottky assumed that the force $F(x)$ is constant between $x = 0$ and $x = x_0$. This corresponds to the force represented by the line NP. Thus the force is

$$F(x) = \frac{e^2}{4x_0{}^2} \tag{34}$$

and by (31)

$$W_0 = \frac{e^2}{4x_0} \tag{35}$$

whence by (32) and (33)

$$W = \frac{e^2}{2x_0} \tag{36}$$

2. Schottky's assumption involves a finite force NO even for infinitesimal displacements of the electron from its normal position O. It is more probable that for small displacements the restoring force is proportional to the displacement, and that for larger displacements it increases to a maximum and decreases again. The simplest assumption of this kind is that represented by the line OP. Thus

$$F(x) = \frac{e^2}{4x_0^{\,2}} \cdot \frac{x}{x_0} \tag{37}$$

which leads to

$$W_0 = \frac{1}{8} \frac{e^2}{x_0} \tag{38}$$

and

$$W = \frac{3}{8} \frac{e^2}{x_0} \tag{39}$$

3. The sharp break in the curve which occurs at P on the above assumption cannot correspond with the true nature of the phenomenon. This objection is avoided if we assume that the force F may be represented by a parabola OVP passing through the origin and tangent to the curve SPT at the point P. The equation of a parabola passing through the origin is

$$\frac{y}{y_1} = 2\frac{x}{x_1} - \left(\frac{x}{x_1}\right)^2 \tag{40}$$

where x_1 and y_1 are the co-ordinates of the point V, the vertex of the parabola.

If we impose the condition that the curve shall have the slope m at the point P (x_0, y_0) we find

$$\frac{x_0}{x_1} = \frac{2 - 2\delta}{2 - \delta} \tag{41}$$

$$\frac{y_0}{y_1} = \frac{4(1 - \delta)}{(2 - \delta)^2} \tag{42}$$

where

$$\delta = \frac{mx_0}{y_0} \tag{43}$$

The area ($OVPx_0$) under the curve OVP may be shown to be

$$W_0 = \int_0^{x_0} y\, dx = \frac{4 - \delta}{6}\, x_0\, y_0 \tag{44}$$

Now by (29) we have

$$y_0 = \frac{e^2}{4x_0^{\,2}} \text{ and } m = -\frac{e^2}{2x_0^{\,3}} \tag{45}$$

whence

$$\delta = -2 \tag{46}$$

Substituting (45) and (46) in (44) gives

$$W_0 = \frac{e^2}{4x_0} \tag{47}$$

Thus

$$W = \frac{e^2}{2x_0} \tag{48}$$

which is the same relation as that obtained on Schottky's assumption *1* (equation 36). Thus the two shaded areas shown in Fig. 3 just balance one another.

By (41) and (42) we find the co-ordinates of the vertex (V) of the parabola to be

$$x_1 = \frac{2}{3}\, x_0 \tag{49}$$

$$y_1 = \frac{4}{3}\, y_0 = \frac{1}{3}\, \frac{e^2}{x_0^{\,2}} \tag{50}$$

By comparing equations (36), (39) and (48), we see that the value of x_0 does not depend very greatly on the particular assumption made as to the law of force when $x < x_0$. From the experimental values of W we should thus be able to calculate approximate values of x_0 with a considerable degree of certainty. Since the third method given above leads to the same equation as that found by Schottky, we shall employ the latter (equation 36) in our calculations of x_0.

The quantity W is the work done in removing a single electron

from a metal. We have previously defined the electron affinity ϕ as the volt equivalent of this work, so that

$$\phi = \frac{W}{e} = \frac{e}{2x_0} \tag{51}$$

Substituting Millikan's value for e (4.774×10^{-10} E.-S.U.) and converting to volts (1 volt = 300 E.-S.U.) this equation becomes

$$\phi = \frac{7.16 \times 10^{-8}}{x_0} \; volts \tag{52}$$

By means of this equation we may calculate the values of x_0 from ϕ.

In Table V the second column contains the data for ϕ obtained by taking weighted means from the values of Table IV. The third column gives x_0 as calculated by equation (52).

It has been found by Bragg (Phil. Mag. (1914) **28**, 355) and Vegard (Phil. Mag. (1916) **31**, 83) that the atoms in crystals of copper and silver are arranged according to a simple face-centered cubic lattice structure. With this arrangement of the atoms it may be readily shown that the shortest distance between adjacent atoms, which may be presented by σ, is given by the relation

$$\sigma = 1.33 \times 10^{-8} \; V^{1/3} \tag{53}$$

where V is the atomic volume (atomic weight divided by density).

We should expect x_0 to be commensurate with σ and for metals which have similar structures it seems probable that x_0 would be approximately proportional to σ. To test this out, the values of σ have been calculated by equation (53), using the atomic volumes given in column 4. Column 5 contains the values of σ while the next column gives the ratios x_0/σ.

It is seen that this ratio is very nearly constant (0.56) for all the elements having atomic weights greater than 60. The values of x_0/σ have been plotted in Fig. 4 against the atomic numbers[25] of the elements as given in column 7. It appears that the ratio increases as the atomic number decreases, particularly in the case of elements of low valency. The following empirical formula

[25] The data on the atomic volumes and atomic numbers used in Table V have been taken from a paper of Harkins and Hall, Jour. Amer. Chem. Soc. (1916) 38, 169.

TABLE V.

1	2	3	4	5	6	7	8	9
Element	ϕ	x_0	Atomic Volume V	σ	$\frac{x_0}{\sigma}$	Atomic Number N	Maximum Valency V	$\frac{x_0}{\sigma}$ Calculated
W	4.52	$1.58.10^{-8}$	9.7	$2.83.10^{-8}$	0.56	74	6	0.56
Pt	4.4?	1.63	9.1	2.78	0.59	78	4	0.56
Ta	4.3	1.66	10.9	2.95	0.56	73	5	0.56
Mo	4.3	1.66	10.7	2.93	0.57	42	6	0.57
C	4.1	1.74	5.5	2.35	0.74	6	4	0.72
Ag	4.1	1.74	10.3	2.90	0.60	47	1	0.62
Cu	4.0	1.79	7.1	2.56	0.70	29	2	0.66
Bi	3.7	1.93	21.2	3.68	0.53	83	5	0.56
Sn	3.8	1.88	16.3	3.38	0.56	50	4	0.57
Fe	3.7	1.93	7.1	2.56	0.75	26	3	0.64
Zn	3.4	2.10	9.2	2.79	0.75	30	2	0.66
Th	3.4	2.10	21.2	3.68	0.57	90	4	0.56
Al	3.0	2.38	10.4	2.90	0.82	13	3	0.72
Mg	2.7	2.65	14.0	3.20	0.83	12	2	0.81
Ti	2.4	2.98	10.7	2.93	1.02	22	4	0.64
Li	2.35	3.04	13.1	3.14	0.97	3	1	1.27
Na	1.82	3.93	23.7	3.82	1.03	11	1	1.07

seems to give values of x_0/σ which are in fair agreement with the experimentally determined values.

$$\frac{x_0}{\sigma} = 0.56 + \frac{0.8}{v}\left(1 - \frac{N}{80}\right)^3 \qquad (54)$$

Here v represents the maximum valence given in column 8. Values of x_0/σ calculated by this equation are tabulated in the

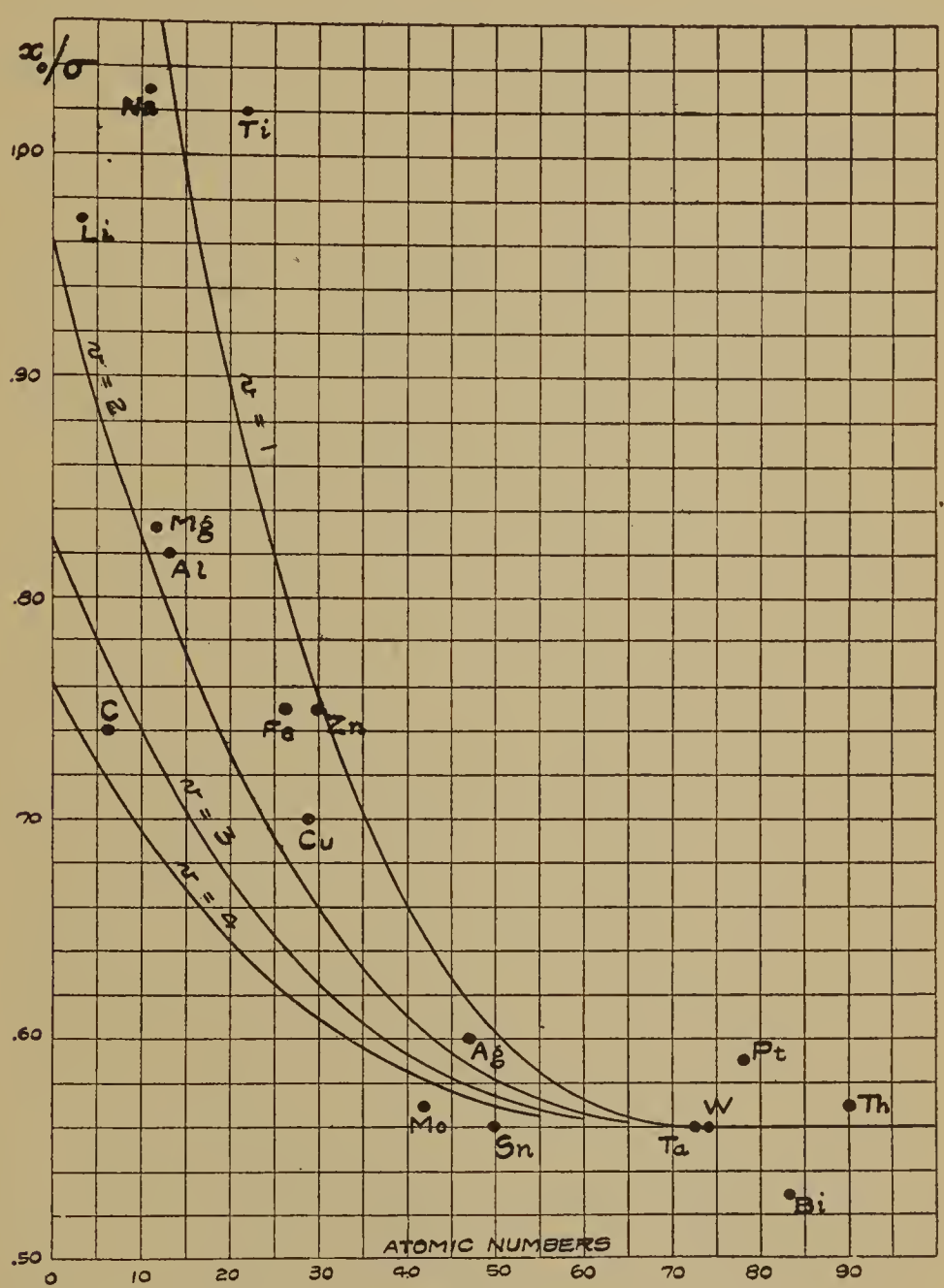


FIG. 4.

last column. Curves obtained by means of the equation for different valencies are also plotted in Fig. 4. In view of the uncertainty in the experimental values of ϕ, too much stress should not be laid on the agreement or lack of agreement of the calculated and observed values.

By means of this formula, however, it should be possible to predict very approximate values of x_0 and therefore ϕ for any metallic element.

For the heavier elements, x_0/σ is approximately constant. From equations (52) and (53) it therefore follows for these elements that ϕ should be inversely proportional to the cube root of the atomic volume. It is interesting to note that Richardson in 1903, in giving values of ϕ for sodium, platinum and carbon, remarks that "These numbers are inversely proportional to the cube roots of the atomic volumes."

This relation acquires a new significance by the method of derivation employed above. Its approximate agreement with the facts must indicate that the attraction of an electron by a metal surface depends, for the heavier elements, only on the size of the atoms. The distances to which the effects attributable to atomic structure extend, is thus proportional to σ the diameter of the atoms. From the numerical value of x_0/σ we may conclude, when an electron is at a distance from a metal surface greater than 56 percent of the diameter of the atoms, that the charge induced by the electron in the metal is substantially the same as if the metal had a continuous structure. On the other hand, according to equation (49), we may estimate that the distance at which the electron is subjected to the maximum attractive force is ⅔ of 56 percent, or 37 percent of the atomic diameter.

This result is so eminently reasonable that it lends strong support to the theory that the larger part of the work done in removing electrons from metals is expended in overcoming the attraction between the electron and its induced image. Although it is possible that electric double layers may exist on pure metal surfaces, the above reasoning makes it probable that such layers can account for only a small part of ϕ.

The increase in x_0/σ for elements of low atomic weight and low valency appears to be perfectly consistent with the above theory. According to Rutherford's and Bohr's theory of atomic structure, atoms consist of a central nucleus having a positive

charge equivalent to N electrons surrounded by one or more rings of negative electrons. The total number of electrons in all the rings is the atomic number N. It is natural that charges should be more easily induced in atoms containing many electrons than in those with few. On the other hand, with atoms containing very large numbers of electrons, the shape or arrangement of the atoms becomes more important than the number of electrons in them. Hence, when N is large, x_0/σ is constant (0.56), but when N becomes small, x_0/σ increases; that is, the effect of the structure extends to relatively greater distances.

The effect of valency may be explained in a similar way. According to Stark's theory, valency is due to "valence electrons" in the outside ring of electrons. We may suppose that these electrons respond particularly easily to disturbing forces. The greater the valency, therefore, the more readily may charges be induced. With elements containing large numbers of electrons, however, valence will be of little importance, since the shapes and arrangements of the atoms will be the determining factor.

The above theory of electron affinity leads us to simple and clear ideas as to the nature and mechanism of contact potentials.

Let us consider the case of two plates of different metals, say zinc and copper, placed parallel to each other a short distance apart. According to Richardson's theory, since ϕ is lower for zinc than it is for copper, electrons will pass from the zinc to the copper until an opposing potential equal to $\phi_{cu} - \phi_{zn}$ develops between the plates.

The question has arisen, whether this difference of potential actually exists between the metals themselves, or whether it originates in surface layers. If the work done when an electron escapes from a metal is wholly due to the attraction of its electric image, then this question may be definitely answered in the sense that the potential actually does exist between the metals. On the electric image theory there is no difference of potential between a metal and the space just outside its surface. A difference of potential between a metal and its surface layer can occur only when a double layer exists, and we have seen that there

is reason to believe that the effects of the double layers are negligible.[26]

Since an electric field exists between the zinc and copper plates when they are in equilibrium, there must be a positive charge on the surface of the zinc and a negative charge on that of the copper plate. If the two plates are now connected by a copper wire, the potential difference will not be changed, for the plates were already in a state of equilibrium.[27]

By bringing the plates together while the wire connects them, the potential difference is maintained, and therefore the electric field between them increases inversely as the distance between them. The electric charges on the surface thus increase. If the two plates are brought into intimate contact a double layer will then exist at the surface of contact.

These relations are illustrated in Fig. 5. There will be a real difference of potential (about 0.8 volt for Zn and Cu) at the junction *AB*. There will be no difference of potential between *C* and *D* nor between *E* and *F*. But in the space *DE* there will be a potential difference equal to that between *A* and *B*.

Suppose we place an inert gas in the gap between *C* and *F* and ionize this gas by a radioactive substance or in any other manner. The positive ions will be drawn to *C* and the negative to *F*. If the surface is covered with a film which prevents the discharge of the ions, the insulating film will be charged (positive at *D*, negative at *E*) on its surface. The double layers thus formed will destroy the electric field between *D* and *E* so that the potential difference which previously existed between *D* and *E* will now occur in the double layers.

[26] Since the atoms in the surface layer of a metal are subjected, in a sense, to unbalanced forces, it is probable that the relative positions of the outer electrons and inner nucleus are somewhat displaced. This would cause a double layer and therefore potential difference at the surface. It is certain, however, that the electric image effect must exist, and since ϕ agrees so well in magnitude with what would be expected on this theory, it may be safely assumed that the effect due to possible double layers may be neglected. As a matter of fact, this assumption only simplifies our ideas, and in no wise does it affect the validity of the conclusions that will be drawn as to the relations between contact potentials and electrochemical action. Of course the potential inside a metal varies from point to point depending on the proximity of electrons and nuclei, so that the term "potential inside the metal" needs very careful definition before use is made of it. In the present case it will suffice to define it as the potential of a point in space just outside of the metal *when no double layers are present* on the surface except those which may be inherent to a pure metal surface.

[27] Richardson assumes this equilibrium is brought about by thermionic emission. Of course this process would be extremely slow at room temperature, but the slowness should not affect the validity of the calculations. According to this view, making contact between the metals is analogous to hastening a chemical reaction by a catalyzer.

But if the ions can discharge themselves on the plates *C* and *F*, then a current will continue to flow as long as the gas continues to be ionized. The positive current will flow from *C* to *A*, *B* and *F*, which is in the same direction as if the copper and zinc plates were separated by dilute sulphuric acid instead of ionized air. If we open the circuit by cutting through the copper conductor at *OP* then a difference of potential will develop between *S* and *T* which will be a measure of the electromotive force of the cell.

The surface *S* will be positively and *T* negatively charged and the difference of potential will be equal to the contact potential between *B* and *A*.

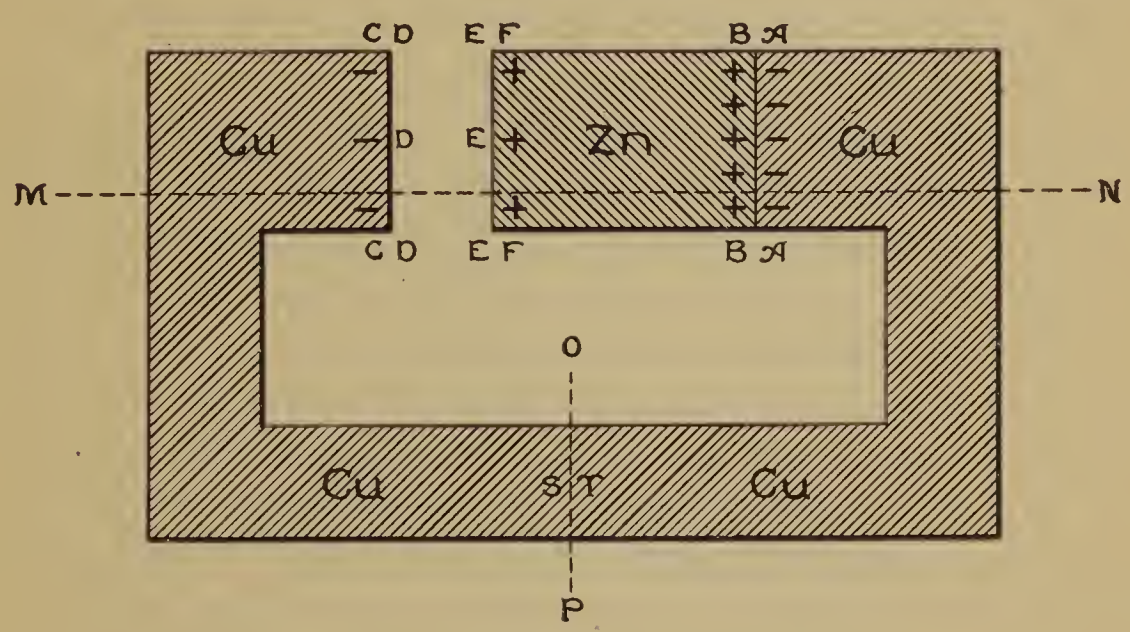


Fig. 5.

Now Lord Kelvin, Greinacher and others have shown that the potentials actually found in this way between the surfaces *S* and *T* are practically the same no matter whether ionized air or acidulated water is placed between the plates *C* and *F*. From this fact, Lord Kelvin concluded that the potential observed with water in the gap was caused by the contact potential, whereas Greinacher concluded that the contact potentials must be caused by the presence of adsorbed water. Since we have the best of reasons for believing that contact potentials exist independently of water films, we must adopt the view of Lord Kelvin that the function of water between the electrodes is similar to that of ionized gas, in that both tend to destroy the field between the metals, and thus allow the contact potential to manifest itself.

The case is so simple when ionized gas is employed that a closer study of it will help to clarify our ideas as to the mechanism of such actions.

If we maintain the gas in an ionized condition, current will continue to flow. This current represents a definite amount of energy per second, equal to the product of the current by the contact potential. Where does this energy come from? Where is the seat of the electromotive force which causes the current to flow?

It is evident that there is no permanent source of energy at the junction of the metals. But it takes energy to produce ionized gas, and this ionization is destroyed by the flow of the current. It is thus clear that the energy of the current is supplied originally by the ionizing agent.

On the other hand, the force which causes the current to flow has nothing to do with the ionization. An electric field exists in the space between the electrodes C and F and therefore the ions move towards the electrodes. It is this field which must be looked upon as the immediate cause of the flow of current. This explains why the energy of the current is proportional to the contact electromotive force and not to the ionizing potential of the gas.

A sharp distinction must be drawn between "difference of potential" and "electromotive force." We have already defined difference of potential as equal to dW/de, that is, as the work per unit charge when the charge becomes infinitesimal. We may now define electromotive force as W/e where W is the work done when an electron (charge e) moves from one place to another. Thus electromotive force is that which tends to cause current (actual electrons and ions) to flow.

We have seen that electrons may be acted on by forces even where no potential difference exists. Thus at the surface of a metal there is an electromotive force equal to ϕ (tending to make electrons flow into the metal), but there is no potential difference. At the contact between two metals, on the other hand, there is a difference of potential equal to $\phi_1 - \phi_2$, but there is no electromotive force. In the free space between the surfaces of two metals there is a potential difference *and* an electromotive force, both equal to $\phi_1 - \phi_2$. This distribution of potentials and

electromotive forces is illustrated in Fig. 6. The broken curve *I* represents the potential and *II* represents the electromotive force when there is a vacuum separating the zinc and copper plates (Fig. 5). Curves *III* and *IV* give similar data for the case when there is ionized gas between the plates. The lettering at the top of the figure corresponds to that of Fig. 5.

The electromotive force of the "cell" obtained by the use of

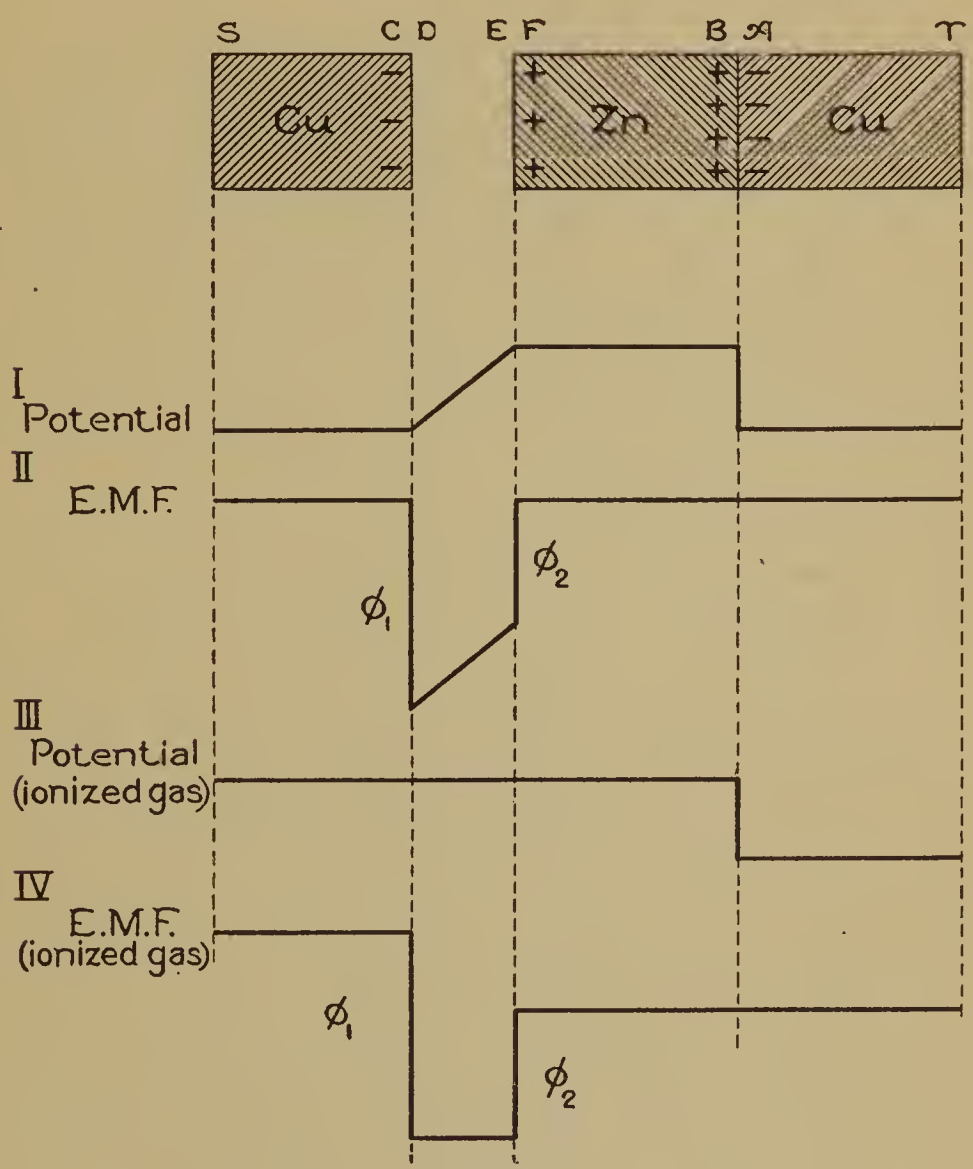


FIG. 6.

ionized gas is located at and between the surface of the plates. The electromotive force between the metals is maintained by the passage of electrons across the junction of the two metals at *AB*. The ionized gas supplies the energy to keep the current flowing. The fact that the electromotive force is produced by an agency that has nothing to do with the source of energy may at first thought appear to be an objection to this theory. But there are many examples of such relationships in nature. Thus the force

which drives a water turbine is the force of gravity, but the energy necessary to maintain the operation of the turbine indefinitely must be derived from the sun's heat which evaporates the water of the oceans. The power obtained from the turbine is directly related to the head of water and the quantity of water used, but is only very indirectly related to the energy consumed in evaporating the water from the sea.

APPLICATION OF THE THEORY TO ELECTROCHEMICAL ACTION.

When the ionized gas between the metal plates (Fig. 5) is replaced by an electrolyte, the potentials remain substantially the same. The effect of the electrolyte is thus to destroy the electric field between the plates, so that the potential difference between the plates no longer balances the contact potential. This action is exactly like that of the ionized gas; but there are, however, certain important differences between the ionized gas and the electrolyte.

The ions of the gas consist of gas molecules which have either lost or gained one or more electrons. When a negative ion strikes the positive electrode it gives up its surplus electron, while the positive ion in striking the negative electrode, takes up electrons. In both cases the ions are converted into ordinary gas molecules.

In the electrolyte, on the other hand, the ions are not charged molecules, but are parts of dissociated molecules capable of permanent existence only while they retain their charges. If these ions are discharged on the electrodes, new substances are produced which are usually very active chemically. Thus if the ions of hydrochloric acid are discharged, atoms of hydrogen and chlorine would be liberated at the electrodes. If these substances can react with the electrodes the current may continue to flow as long as the supply of active materials holds out. On the other hand, if the electrodes are not attacked, then the discharged ions will be forced by the electric field to form double layers on the electrodes which will oppose the flow of current. The cell will thus become polarized. In order to prevent this polarization it is essential that some chemical reaction shall take place to remove the products that would otherwise accumulate and form double layers at the surfaces of the electrodes. The chemical reaction supplies the energy by which the action is maintained, but it does

this by removing a force which otherwise opposes the contact electromotive force. The fact that the energy is derived from a chemical reaction does not indicate that the electromotive force of the cell is caused by chemical action.

This will be made clear by an analogy. Let us imagine a deep hole in the ground, near the shore of a lake. A pipe conveys water from the lake to a water turbine placed at the bottom of the hole. If the turbine is operated, power is generated, but only for a short time, for the well soon becomes filled with water. The water pressure at the turbine remains the same as before, but its effectiveness is removed by an equal and opposite pressure at the outlet side of the turbine. In order to continuously obtain power from the turbine it is necessary to pump the water from the well back to the level of the lake. The function of the pump is to supply the energy by which the back pressure on the turbine can be removed. Since there is no direct connection between the pump and the turbine we cannot say that the flow of water through the turbine is "caused" by the pump. Yet to obtain power continuously from the turbine, requires the expenditure of at least an equal amount of power at the pump.

In this analogy the pressure of the water at the turbine corresponds to the contact electromotive force. The pump corresponds to the chemical reactions. When there are no chemical reactions (pump), the electromotive force (pressure) can cause current (water) to flow only for a short time, since a polarization (back-pressure) soon develops which prevents the flow of current. By means of chemical reactions (the pump), polarization (back-pressure) may be prevented so that current flows and power may be generated continuously. The potential energy stored in the lake corresponds to the heat energy stored in the electrons in the metals.

Let us return to the comparison of the electrolytic cell with the ionized gas cell. The ionization of a gas requires the expenditure of relatively large amounts of energy, as is indicated by the large ionizing potentials, 5 to 20 volts. An ionized gas is therefore in an unstable condition. The energy that can be obtained from an ionized gas cell is derived from the free energy of recombination of the ions. There is no necessity for any attack of the electrodes in such cells.

With electrolytic cells, on the other hand, the dissociation of the electrolyte represents an equilibrium condition, so that no free energy can be obtained by the recombination of ions. The maintenance of current in such cells must therefore be due to chemical reactions.

From what has been said about the attack of metal by discharged anions it should not be inferred that the contact theory precludes the direct formation of positive ions from the metal of the electrodes. Of course if positive ions do leave the metal, then it becomes unnecessary for anions to be discharged. Either viewpoint is consistent with the contact theory.

Electrode Potentials.

In a cell of the type illustrated in Fig. 5, we have seen that relatively large differences of potential may be developed between S and T (see also Fig. 6), even when no difference of potential occurs between the two electrodes C and F. It is not possible to assume, however, that all the electromotive force of an electrolytic cell is caused by the contact electromotive force. It is a demonstrated fact that the E. M. F. of cells varies with the electrolyte used, while the contact potential, being an intrinsic property of the metals, cannot depend on the electrolyte. It is clear, therefore, that there must be potential differences between the two electrodes which depend on the concentrations of the solutions used.

But these potential differences are in general very much smaller than those calculated by the usual method, in which contact potentials are neglected. In Table VI the second column contains the electrode potentials ϵ_h as given by the usual method.[28]

These values represent the potentials of the metals in solutions of their salts containing normal ion concentration, and are calculated on the assumption that there are no contact potentials at the junction of the metals. The potentials are referred to that of the hydrogen electrode as the zero point. In the third column are the values of ϕ taken from Table V.

[28] The data for Li and Na are those given by Lewis and Argo, J. Am. Chem. Soc. (1915) **37**, 1983. The rest of the data were obtained from "Messungen elektromotorischer Kräfte," Abhandlung deut. Bunsen. Ges. **2** (1911).

TABLE VI.

Electrode Potentials and Contact Potentials.

Element	Electrode Potential ϵ_h	ϕ	$\phi - \epsilon_h$	True Electrode Potential Σ^h
Ag	+0.80	4.1	3.30	+0.40
Cu	0.34	4.0	3.66	+0.04
Bi	0.20	3.7	3.50	+0.20
Sn	—0.10	3.8	3.90	—0.20
Fe	—0.43	3.7	4.13	—0.43
Zn	—0.76	3.4	4.16	—0.46
Mg	—1.55	2.7	4.25	—0.55
Li	—3.03	2.35	5.35	—1.65
Na	—2.73	1.82	4.55	—0.85

If the electromotive force of a cell were dependent entirely on the contact electromotive force, then the differences between values of ϵ_h for any two elements should be the same as the differences between the corresponding values of ϕ. In this case $\phi - \epsilon_h$ would be the same for all the elements. As a matter of fact (see column 4), these values are not constant, but show a distinct tendency to increase as we go towards the electropositive end of the series. By decreasing these results by 3.7 volts we obtain the values given in the last column. These represent the electrode potentials (arbitrary zero point) after correcting for the contact potentials. It is seen that these are on the average a little less than half the potential differences obtained when contact potentials are neglected (2d column). On this basis we might conclude that contact electromotive forces can account for only about half of the observed electromotive forces of cells. The accuracy of the data, however, is not sufficient at present to justify such a conclusion. It is probable that the values of ϕ for the more electropositive elements are much more affected by the presence of surface films than in the case of the more electronegative elements. Such surface films tend to make the metals appear more electronegative. The contact electromotive forces characteristic of pure metal surfaces will probably be found to be greater than the values thus far determined. In comparing electrode potentials with contact potentials the data should be corrected for the electromotive forces occurring at the junction of the normal solutions which are assumed to surround the various electrodes. Again,

it must be remembered that the electrode potentials vary with the concentrations of the electrolyte, whereas the contact potentials do not. It is therefore uncertain at what concentrations comparison should be made.

Unfortunately, the lack of sufficiently reliable experimental data makes it impossible at present to determine the true electrode potentials with an accuracy comparable with that attained in ordinary electrochemical measurements.

"Absolute" Electrode Potentials.

The electrode potentials which we have considered above have been referred to an arbitrary zero point. Several methods have been proposed (Nernst, Palmaer, Billiter, etc.) to determine the so-called absolute potentials of the electrodes; that is, the actual potential difference between an electrode and the surrounding electrolyte. So far, these determinations have led to wholly inconsistent results which have never received adequate explanation. It seems quite possible that these difficulties have been largely due to the neglect to take into account the contact potential differences at the junction of the metals. The writer hopes to take up this question in detail in a future paper, in which he also expects to discuss the phenomena of electrical endosmosis.

Electrochemical Equilibrium and Kinetics.

The electromotive forces of various simple cells may be calculated with satisfactory accuracy from the ordinary electrode potentials by means of Nernst's equation. It may therefore be asked, what is the use of splitting these electrode potentials up into two parts—one due to contact potential and the second to other causes—when in actual calculations of the electromotive force the two parts must be added together again? The consideration of contact potentials seemingly only complicates matters, without adding any new elements of importance.

This objection is perfectly valid so long as we consider only the total electromotive forces of reversible cells. The Nernst equation is only a statement of a thermo-dynamic relation and applies strictly only to reversible equilibrium conditions. Such relations can tell us nothing whatever of the mechanism or kinetics of a process. Similarly, the ordinary electrode potentials

give us the net result obtained with various combinations of electrodes under equilibrium conditions. Such values give us little information about the real mechanism of the cells or their operation when current actually flows.

It is true that the greater part of the work of the electrochemist until recent years has been devoted to the study of just such equilibrium conditions. In this limited field thermodynamics is rightly considered to be the guiding principle. Thermo-dynamics, however, tells us practically nothing of the kinetics or mechanism of any process.

The attention of the electrochemist is being forced more and more to the consideration of kinetic phenomena, such as overvoltage and passivity. In these fields the progress of our knowledge has been notoriously slow. Although vast numbers of papers have been published and multitudes of theories have been advanced, it is generally agreed that we have no clear understanding of the nature of these phenomena nor knowledge of the underlying laws. The slowness of this progress has probably been largely caused by an undue emphasis on what may be called the thermo-dynamic viewpoint in electrochemistry.

In order to make more rapid progress in the kinetics of electrochemistry it will be essential to consider the mechanism of these processes according to the methods which have had such revolutionary effects in the recent developments in physics. That is, we must regard these phenomena from the viewpoint of the kinetic theory and apply statistical methods wherever possible. We must know how the individual ions and atoms pass from the electrode into the solution, or *vice versa,* and must know something definite about the structure of the double layers which are the cause of the potential differences occurring at the surfaces of the electrodes. In other words, we must study the detailed mechanism of electrochemical action.

In this paper the attempt has been made to show that contact potential at the junction between metals is one of the factors which must be taken into account in reaching any understanding of the mechanism of electrochemical action.

In subsequent papers it is planned to discuss other phases of the mechanism of these actions and to apply the results to the consideration of such phenomena as overvoltage and passivity.

SUMMARY.

1. The history of electrochemistry has been marked by a century-long conflict between the contact theory and the chemical theory of electrochemical action. The modern electrochemist usually considers that this conflict has long been brought to a close by the victory of the chemical theory. He believes that contact potentials between metals are entirely inappreciable. No such uniformity of opinion has existed among physicists.

2. Within the last few years very remarkable work in physics has demonstrated that contact potentials of large magnitude do exist, even between pure metals in a practically perfect vacuum. This evidence, which is reviewed in some detail, has been obtained by the study of *1,* Electron emission from heated metals; *2,* Photoelectric phenomena; *3,* Contact potentials. Several independent methods lead to values of the contact potentials which are in substantial agreement.

3. Much of the difficulty which the electrochemist has had in reconciling the contact theory with the known intimate relation between chemical action and electrochemical phenemona, has been due to failure to properly define "potential difference" and "electromotive force." Definitions of these are given, and a theory of the mechanism of the effect is developed.

4. It is not necessary to take into account contact potentials when only the electromotive forces of reversible cells are considered. But in dealing with the kinetic phenomena, such as overvoltage and passivity, or with effects due to single potential differences, the contact potentials must be an essential factor. The detailed consideration of these relations is reserved for a future paper.

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DISCUSSION.

C. McC. Gordon: I would like to get more light on one or two questions. I understand that between two metals in a vacuum there is a certain definite contact-potential which is determined by the metals alone. What I did not understand from the paper was whether, when you place two metals very closely together, hammer or squeeze them together, the contact-potential would be the same as when both metals are in a vacuum.

To my mind we should not expect the same contact-potential. At each metal-vacuum surface there is an electromotive force, the size of which is determined by the configuration and distance apart of the electrical particles of the atom. But when the vacuum is replaced by a second metal the surface conditions are entirely changed.

Irving Langmuir: The potential difference does exist when the metals are in contact. When the metals are not in contact, you cannot say anything at all about the potential difference between them, because in the case of two metals out of contact everything depends on their past history. You can have two metals in a vacuum at 1,000 volts difference of potential, you can leave them in a high vacuum, separated from one another, and they will retain their charges indefinitely, so that you cannot say that the difference in potential between two metals separated from one another has any definite value whatever until you provide some means by which they may reach a condition of equilibrium with one another. This equilibrium may be brought about by placing them in contact, or by any one of a dozen ways, for instance, by bringing one of them in contact with a hot filament, which will give off electrons.

Richardson and Debye have shown that the law of conservation of energy requires that the difference of potential between two metals in contact be the same as the difference in potential they will reach when they are brought in contact with bodies which emit electrons.

The whole essence of this work is that the difference of potential must exist when they are in intimate contact.

F. C. Frary: Would we be correct in concluding that what we measure as electromotive force in a thermo-couple is really a measure of the temperature coefficient of these contact electromotive forces?

Irving Langmuir: Yes.

F. C. Frary: Is this contact potential a function of the molecule? Do you not have some similar effect from the molecules, such as undissociated salts in solutions, and when you have a contact potential between two solutions is it due only to the difference in mobility of the ions as generally stated, or would the molecules there have to be considered also?

Irving Langmuir: I have not thought much about the contact potential between two solutions, but I feel very skeptical about the accuracy of the formulas derived in the past.

In regard to the first point, that was answered by Lord Kelvin, in the first days of his work on the subject, in which he showed that you do not have to accept Maxwell's view that the Peltier effect was a direct measure of the contact potential, but he showed from thermo-dynamic reasons that the Peltier effect was a measure of the temperature coefficient. Since the Peltier effect is small, you may conclude that the temperature coefficient is small, which is in accord with Milliken's recent work.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

CONTACT RESISTANCE OF METAL ELECTRODES.

By N. K. Chaney.

In some unpublished work the writer has shown that under certain conditions a high "contact resistance" exists between the surface of an electrode of sheet zinc and the electrolyte. This paper proposes to give a resumé of some of the characteristic properties of this resistance, followed by an explanation or theory of its origin and the experimental evidence upon which the theory is based.

Characteristics of the Contact Resistance.

(1) The "contact resistance" between zinc and an electrolyte of zinc chloride and ammonium chloride is a secondary development occurring with measurable rapidity after the immersion of the zinc in the electrolyte. At the instant of immersion it is very small. It may rise to values of from 200 to 400 ohms per square inch (1,250 to 2,500 per sq. cm.) of electrode surface.

(2) It forms the principal part of the internal resistance of dry cells at low current drains, and as determined by measurements upon the latter it has a high temperature co-efficient, decreasing to one-tenth of its value with a temperature rise of from 0° to 45° C. It is this contact resistance of the zinc electrode which was measured by Carhardt in his resistance measurements upon the early Gassner dry cells, and which caused the rapid rise in his resistance curves at low current densities.[1]

(3) It is lessened or destroyed temporarily by current densities above certain low limiting values, being practically unaffected by currents of less than 1 milliampere per 50 square inches (315 sq. cm.) of electrode surface,[2] even if continued for a considerable time. With higher current densities it begins to rapidly de-

[1] Phys. Rev. (1894-5) **2**, 392; (1898) **7**, 193.

[2] 50 square inches (315 sq. cm.) is the approximate area of a 6-inch (15 cm.) dry cell.

crease, and becomes negligible at current densities of about 1 ampere per 50 square inches (315 sq. cm.). Upon open circuit the resistance again slowly rises toward its initial value.

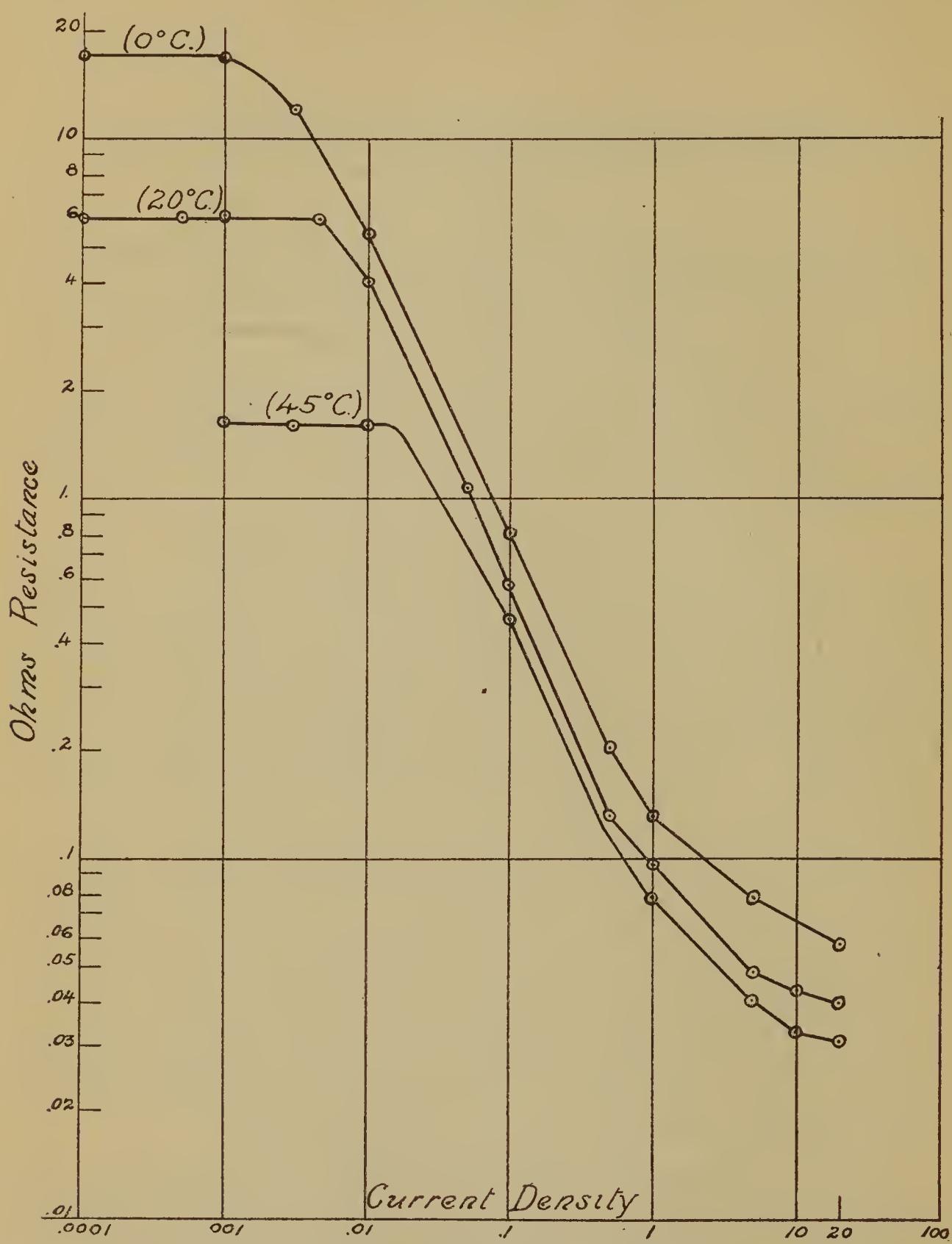

FIG. I. Change in Internal Resistance of 6-inch (15 cm.) Dry Cells, with Current Density, at Temperatures Indicated.

(4) It is destroyed or very greatly reduced by chemical treatment of the zinc surface, *e. g.*, by corrosion with dilute sulphuric acid.

The data showing these facts are summarized in the tables following. The curves from Table I, plotted on a logarithmic scale in Fig. 1 are similar to Carhardt's curves, but being extended to much smaller current densities show the limiting values in the rise in resistance at low current densities.

TABLE I.

Testing current in amperes.	Change in resistance with current density and temperature. Resistance in ohms per 6-inch (15 cm.) Dry Cell. 0° C.	20° C.	45° C.
0.0001	17.5	6.0	...
0.001	18	6	1.7
0.003	12	6	1.6
0.005	...	6	...
0.01	5.25	4	1.6
0.05	...	1.1	...
0.10	0.81	0.56	0.46
0.50	0.21	0.147	...
1	0.137	0.0097	0.081
5	0.078	0.049	0.041
10	....	0.044	0.033
20	0.059	0.040	0.031

The fact that the resistance curve becomes practically flat below a certain limiting current density was checked by carefully repeated measurements, as the following will show.

TABLE II.

Testing Current.	Resistance of Standard Dry Cell at 20° C.
0.0012 ampere	5.7 ohms
0.0006 "	5.9 "
0.000075 "	6.0 "

TABLE III.

Change in resistance with time of immersion.

(Resistance measured between two zinc electrodes 50 square inches (315 sq. cm.) in area, immersed in zinc-ammonium chloride electrolyte.)

Time after immersion.	Resistance in ohms.
0 minutes	0.42
1 "	1.55
3 "	1.92
10 "	3.70
20 "	4.0
4 days	4.0 to 11.0
After corrosion in H_2SO_4	0.40

TABLE IV.

Change in resistance of dry cell with age.

Age of Cell.	Resistance in ohms.
2 hours	2.0
20 "	14.0
4 days	7.2
9 "	4.3

The resistance in the dry cell rises in a similar manner to that in the zinc electrodes, after which it begins to fall. This latter effect is doubtless due to surface changes similar to the effect of corrosion with acid, but not proceeding to the same extent.

Between two zinc electrodes of 1 square inch (6.3 sq. cm.) surface a resistance from 400 to 750 ohms is found, or 200 to 375 ohms per square inch (1,260 to 2,350 per sq. cm.) per electrode.

The question arises, what is the change which occurs at the zinc surface, or what manner of high resistance layer is developed by the interaction of the zinc and the electrolyte?

The present hypothesis is that this contact resistance is due to a hydrogen layer or film, discharged upon the zinc by local action.

That hydrogen is so deposited upon the zinc in a neutral electrolyte is well known from the fact of its final evolution in the form of bubbles, the rate of its evolution depending upon the temperature and the purity of the zinc and the electrolyte respectively. According to this theory the contact resistance depends upon the properties of this hydrogen film, its thickness, its physical state of aggregation and dissociation on the electrode surface, and its molecular and ionic equilibria with the electrolyte. It is these properties of the hydrogen film which are affected by current density, temperature, and by such physical characteristics of the electrode surface as its smoothness, porosity, adsorbtive power, etc.

The evidence for this view may be summarized as follows:

(*1*) If there is actually a hydrogen layer over the zinc surface it should behave substantially as a hydrogen electrode at such current densities as do not materially disturb the film.

Inert and passive electrodes such as platinum must behave as gas electrodes, their polarization phenomena depending entirely upon the occluded and adherent gases (hydrogen, oxygen, etc.).

Now at extremely low current densities the resistance between a pair of smooth fresh zinc electrodes is practically the same as that between smooth platinum electrodes of the same dimensions (about 600 to 800 ohms between two electrodes 1 inch (2.5 cm.) square). This similarity in resistance suggests a common cause, *i. e.*, that the zinc electrodes are behaving at low currents as passive, inert electrodes, the current being transferred between electrode and electrolyte by hydrogen ions from the gas film rather than by zinc ions.

(*2*) Conditions or treatment which would be expected to destroy or disturb a hydrogen film have a corresponding effect upon the observed contact resistance.

The experimental observations in support of this statement are:

(*a*) The gradual increase in resistance after contact with the electrolyte corresponds with the progressive formation of a hydrogen film by electrochemical action, as does also the gradual recovery of the resistance after its destruction by heavy currents.

(*b*) Treatment of the electrodes in a manner to disturb or destroy a hydrogen film, as by agitation of electrode, by exposure to air, and by rubbing the electrode surface, are all found to temporarily lower the resistance, which recovers more or less rapidly when again undisturbed.

(*c*) The breaking down of the resistance by heavy current drains is a result which would be also predicted for the hydrogen films. The hydrogen layer upon such electrodes must suffer a constant loss by solution and diffusion in the electrolyte. This loss must be made good by the ionization and solution of more zinc, and the discharge of the resulting hydrogen upon the electrode surface. If now a considerable difference in potential is set up between two zinc electrodes, the renewal of the hydrogen film by local action will be decreased at both electrodes, for the following reasons: The higher negative charge on the cathode will oppose further ionization and solution of zinc and the consequent discharge of hydrogen will be prevented. The higher positive charge on the anode will oppose the further discharge there of hydrogen ions. Hence the hydrogen film will be diminished or destroyed at both anode and cathode by the normal diffusion losses, when a difference in potential is maintained between them.

This loss of the hydrogen film by diffusion will thus occur equally at both anode and cathode. With the passage of current, however, there will be a direct tendency for the hydrogen at the anode to be ionized and migrate to the cathode. This would tend to destroy the hydrogen film at the anode more rapidly, and to replace part of the cathode losses.

The hydrogen film theory of the "contact resistance" therefore suggests that with appreciable current drains the resistance at the anode should be less than at the cathode, and should be more rapidly destroyed at the anode by the passage of current. This expectation has been quite generally verified. The experiments indicate that the anode resistance is the first to be broken down, and is in general lower than the cathode resistance at higher current densities. Also that rubbing or agitating the anode has a greater effect in reducing the combined anode-cathode resistance than has a similar treatment of the cathode, since the re-forming of the hydrogen film is hindered by the electrolyte action of the testing current to a greater extent at the anode than at the cathode.

Experimental Results.

A more detailed consideration of the experimental evidence for the above statements will now be taken up.

The experimental part of the work has consisted in the measurement of the resistance between various pairs of metal electrodes immersed in a common electrolyte. The changes in this resistance with changes in current density, with the time and amount of current passed, and with changes in the environment, condition, and chemical or physical treatment of the electrodes, were measured.

The method of determining the resistance consisted broadly in passing a direct current between the electrodes and measuring the potential drop, correction being made for the counter E. M. F. of polarization. The exactness with which the polarization E. M. F. could be determined by the method employed was found to depend largely upon the nature of the electrodes. With zinc, mercury, and to a lesser extent with platinum, the polarization values were sufficiently definite and constant so that clean-cut readings could be obtained. With lead electrodes, upon the

other hand, the polarization values changed so rapidly that no definite determination was possible. Polished iron electrodes when fresh gave definite polarization values, but after a little current had been passed through them they behaved like lead. Where definite determination of the polarization E. M. F. is not possible, the resistance values of course are erratic and meaningless.

In some cases, where the separate changes at anode and cathode were to be followed, a third or exploring electrode was used and the resistances between it and the primary anode and cathode respectively were measured. The sizes and arrangements of the electrodes vary in the different experiments. Their surface area is given and the current used in making the resistance measurements is stated for each general arrangement. In any given experimental arrangement the resistance of the electrolyte is constant, and forms the zero point of the "contact resistance." That is the latter is the resistance over and above that of the electrolyte proper.

Experiment I.

Arrangement: Two zinc electrodes, 2 square inches (12.5 sq. cm.) in area, placed in porous cups. Cups placed in battery jar containing 20° Bé zinc chloride solution saturated with ammonium chloride and filled with the same solution. Resistance measured with 0.001 ampere current.

Test No.		Resistance.
1.	Initial total resistance between zinc electrodes	96 ohms
2.	Residual resistance after passing half an ampere for one minute between electrodes	4 "
2a.	Resistance of electrolyte between electrodes, or zero point of the contact resistance	3 "
3.	Replaced anode with fresh electrode, leaving cathode undisturbed	15 "
4.	Passed 0.5 ampere 1 minute between new anode and old cathode	4 "
5.	Replaced cathode with fresh zinc. Anode left undisturbed	81 "
6.	Replaced cathode used in test 5 with old cathode used in tests 1 to 4	12 "

The data show that one minute at this current density has almost completely destroyed the high contact resistance. The resistance of electrolyte and porous cups alone is 3 ohms, as shown in test *2a.* The total resistance between the regular electrodes

has been reduced to 4 ohms, hence the "contact resistance" has been reduced from 93 ohms to 1 ohm (the "contact resistance" being 96 — 3, and 4 — 3 ohms respectively, before and after the passage of the current).

If we assume in tests *3* and *5* that the contact resistance is wholly due to the fresh electrode, which is approximately true since the contact resistance of the used electrode has been reduced to a very small quantity, then in test *3*, with the fresh anode and the used cathode the contact resistance of the anode is 15 — 3, or 12 ohms, and for the used anode and fresh cathode the resistance is 81 — 3, or 78 ohms. Hence the sum of the contact resistances of fresh anode and cathode calculated from tests *3* and *5* is 90 ohms, which approximates to the value of 93 ohms calculated from tests *1* and *2a* with the original pair of zincs. (It should be noted that these two values are obtained with *two independent sets of electrodes,* by direct comparison in the first case, and by indirect comparison in the second. Hence the agreement is reasonably good.)

Thus the contact resistances of anode and cathode are in the ratio of 12 ohms to 78 ohms. That is, with a current of about 0.001 ampere per 2 square inches (12.5 sq. cm.) of electrode surface, the contact resistance of anode is about 15 percent and that of the cathode 85 percent of the total contact resistance. This would mean either that the film was broken down to a greater extent at the anode, as predicted, or else that the resistance of the film was to a large extent uni-directional, and depended upon whether the current was entering or leaving the electrode.

Experiment II.

Same arrangement as *Experiment I,* with exploring electrode in addition. Let *A* and *B* be the two primary electrodes and *X* the exploring electrode.

1. Passed 0.5 ampere 1 minute from *A* to *B*.

(*a*)	Resistance between *A* and *B*	3 ohms
(*b*)	" " *X* " *A*	10 "
(*c*)	" " *X* " *B*	15 "

That is, the resistance between a third neutral electrode and the anode was less than that between the neutral electrode and the cathode.

2. After 10 minutes open circuit the resistances were as follows:

(*a*)	Between *X* and *A*	25 ohms
(*b*)	" *X* " *B*	56 "

That is, the cathode was recovering its high resistance more rapidly than the anode.

3. The electrodes *A* and *B* were now reversed. A current of 0.5 ampere for one minute was passed from *B* to *A*.

(*a*)	Resistance between *B* and *A*	3 ohms
(*b*)	" " *X* " *B*	6 "
(*c*)	" " *X* " *A*	10 "

In this case, although the resistance between *A* and *B* is still 3 ohms the relative resistances of *A* and *B* to the neutral electrode have been reversed, the primary electrode which is made cathode having in each case the relatively higher resistance against the third electrode. The contact resistance in 1(a) and 3(a) has been completely destroyed, but in the time elapsing before measurements (*b*) and (*c*) it has begun to recover, and at a faster rate at the cathode than at the anode.

Experiment III.

Same arrangement as *Experiment II,* using new electrodes. *A* and *B* primary electrodes, *X*, exploring electrode.

1	Resistance between *A* and *X*	118 ohms
	" " *B* " *X*	118 "
2	Passed current of 0.5 ampere 1 minute from *A* to *B*.	
	Resistance between *A* and *X*	50 ohms
	" " *B* " *X*	75 "

Here again the electrode which is made the anode shows a lower resistance against a neutral electrode than one which is made the cathode.

The experiments thus far have indicated that with relatively high current densities the anode resistance has a lower value or falls more rapidly than the cathode resistance.

If relatively larger electrodes are used, with correspondingly lower current densities, the resistance may be unaffected, and the distinction between the anode and cathode affect tend to disappear. There remain only the individual peculiarities of the electrode, and the results are accordingly more irregular.

Experiment IV.

Arrangement: Primary electrodes are 6 by 8 inch (15 by 20 cm.) battery zincs immersed one-half inch (1.25 cm.) apart in zinc and ammonium chloride solution. Resistance measurements made with current of 0.002 ampere.

With these electrodes the resistance rises rapidly for 5 or 10 minutes after immersion, and thereafter is subject to more or less arbitrary variations. Hence comparative measurements must be taken while the electrodes are in a fairly stable condition.

		Resistance
1	Resistance between electrodes *A* and *B* after 10 minutes.....	3.7 ohms
	A is anode and *B* is cathode for the testing current.	
2	Removed *B* and washed with distilled water. Replaced it....	3.2 "
	After 10 minutes	3.5 "
3	Removed *B* again. Washed and rubbed dry	3.0 "
	After 10 minutes	3.2 "
4	Removed anode *A*, dried and replaced it	1.5 "
	After 15 minutes	3.0 "

If the resistance is due to a film of hydrogen, removing the electrode and exposing it to the air in this manner would be expected to destroy the film and lower the resistance.

Cleaning the anode also has a much more pronounced effect than cleaning the cathode. That is, under these conditions and with very low current density, the film on the cathode seems to be partially restored by the testing current itself almost immediately, whereas the restoration of the film on the anode is much slower. This is quite consistent with the behavior to be expected of hydrogen films at anode and cathode respectively. The films should be destroyed more rapidly at anode than at cathode, and conversely, if conditions permitted the re-formation of the films, this should take place more rapidly at cathode than at anode, for the reasons originally stated.

The mere agitation of the electrode in the electrolyte should also tend to disturb a film of this kind, both by removing it mechanically and by causing it to dissolve more rapidly in contact with fresh unsaturated electrolyte. This is found to be the case. Here also the agitation of the anode has a much more pronounced effect than the agitation of the cathode.

Experiment IV. (Continued)

		Resistance	
5	Resistance between *A* and *B* after steady equilibria was reached	3.7	ohms
6	Agitated *B* (cathode to testing current)	2.8	"
7	Agitated A (anode to testing current)	1.5	"
8	After equilibrium (10 minutes)	3.7	"
9	Removed both *A* and *B* from electrolyte, exposed to air 10 seconds and replaced them	1.2	"
10	After replacement for 10 minutes	3.7	"
11	Corroded electrode *B* with H_2SO_4. *A* (anode), *B* (cathode)	1.55	"
12	*A* (cathode), *B* (anode)	1.55	"
13	Both *A* and *B* corroded with H_2SO_4	0.07	"

Test 13 with corroded plates is put in to show that the resistance of the electrolyte is negligible compared to the contact resistance of the normal electrodes.

Since a corroded electrode has practically no contact resistance, substituting a corroded electrode for one of the uncorroded electrodes should give the contact resistance of the other uncorroded electrode.

Tests 10, 11 and 12 show that electrode *A* under the conditions above had a contact resistance of about 1.5 ohms, somewhat less than half of the combined contact resistances of *A* and *B* together. Furthermore, the resistance of *A* was the same whether it was made the anode or the cathode of the testing current, indicating that at this low current density the hydrogen film was not greatly disturbed and the resistance of the film to currents whether entering or leaving the electrode was the same. The earlier experiment, (I), had indicated that, with higher current densities, the resistance of the anode was lower than that of the cathode.

This different behavior at different current densities is consistent with the character of the resistance curve with changing current. Higher current densities break down the resistance (and break it down more rapidly at anode than at cathode). Current densities below a certain minimum value do not affect the resistance at all, and therefore there is no reason why the direction of the current should make any difference, or the anode behave in a different manner from the cathode.

Experiment V.

Arrangement same as *Experiment IV.*

The resistance between a normal electrode *A* and a corroded electrode *B* was measured with low and high current densities, for both anode and cathode positions of *A*.

							A as anode.	A as cathode.
	Testing	current	0.002	amp.	Resistance	.....	1.4	1.4
a	"	"	0.01	"	"	.....	1.33	1.37
b	"	"	0.1	"	"	.....	0.46	0.30
	"	"	(0.1)	"	"	.....	(0.45)	(0.31)
	"	"	1.0	"	"	.....	0.078	0.085
c	"	"	(1.0)	"	"	.....	(0.0785)	(0.085)

This agrees with the previous experiment, in that the resistance is independent of the direction of the current at low densities and with high current density the resistance is higher when the electrode *A* is cathode than when it is anode. At 0.1 ampere per 50 square inches (315 sq. cm.) of electrode surface the anode seemed to have a definitely higher resistance than the cathode. The figures in parenthesis are the check values upon duplicating the measurements.

The cause of this irregularity is not explained, but it appeared only when the testing current was initially passed through the electrode. If this same current density was maintained continuously, then the resistance rose when the uncorroded electrode was cathode and fell when it was anode, as expected.

This is shown in the next experiment.

Experiment VI.

Arrangement as in *Experiment IV.*

1. Passed testing current of 0.1 ampere, for time indicated, from *B* (corroded) to *A* (uncorroded.)

Time	Resistance
0 minutes	0.27 ohm
1 "	0.27 "
2 "	0.30 "
3 "	0.36 "

2. Reversed direction of testing current, making *A* anode.

0 minutes	0.38 ohm
1 "	0.24 "
3 "	0.21 "

3. Reversed testing current again making *A* the cathode.

0 minutes	0.21 ohm
1 "	0.27 "
2 "	0.33 "

The previous experiments have indicated that in using a plain zinc electrode against a corroded electrode, the contact resistance of the zinc electrode was the same irrespective of the direction of the current, at very low densities. This is not true at higher current densities and the transition point seems to vary with the individual electrodes.

In Experiment VII two electrodes were allowed to stand for a couple of days in the electrolyte. The corroded zinc became covered with hydrogen bubbles. The testing current was 0.002 ampere.

Experiment VII.

Arrangement as in *Experiment IV.*

Resistance between *A* (uncorroded) and *B* (corroded.)

1	Resistance with *A* as anode	1.55 ohm
2	" " " " cathode	1.76 "
3	" " " " anode	1.55 "
4	" " " " cathode	1.76 "

Here, even at very low current density there is a distinct difference between anode and cathode resistance.

The resistance between a corroded and an uncorroded zinc electrode under the conditions of these experiments has been considered as wholly due to the contact resistance of the uncorroded electrode, the resistance of the electrolyte and of the corroded zinc being considered relatively negligible.

That this is substantially so is illustrated by a few measurements in which pairs of uncorroded electrodes *A, B, C, D,* etc. and a corroded electrode *X* are used, *X* being of small size and placed between *A* and *B*.

Experiment VIII.

Primary electrodes as in *Experiment IV*, with small corroded electrode between.

1	Resistance between *A* and *B*		3.0 ohms
	" " *A* " *X*	1.05	"
	" " *B* " *X*	1.92	"
Calculated resistance of *A* and *B* if resistance of *X* is zero			2.97 "
2	Resistance between *C* and *D*		3.25 ohms
	" " *C* " *X*	1.05	"
	" " *D* " *X*	2.15	"
Calculated for *C* and *D*			3.25 "
3	Resistance between *E* and *F*		8.2 ohms
	" " *E* " *X*	6.18	"
	" " *F* " *X*	2.15	"
Calculated for *E* and *F*			8.3 "

The above data also show that the resistance of the hydrogen films upon different zinc surfaces is subject to very large variation. There was no known difference in the previous history of electrodes *E* and *F*, yet *E* developed three times the resistance of *F*.

The experimental data given herewith are of an approximate character, designed to show the general order of quantitative differences. A study of the nature of the individual variations peculiar to different metal electrodes under more refined conditions will be of much interest, and the extension of the investigation to a more complete study of other metallic electrodes promises a real advance in our knowledge of what is going on at the electrode surface, and may be expected to throw additional light upon the related problems of over-voltage, electrode polarization, etc.

For example the contact resistance between pure mercury electrodes is initially much lower than that between two smooth zinc electrodes, but it *rises* with the continued passage of current, whereas that of the zinc electrodes *falls*. Hence a more complete study of various metals is necessary.

It may be suggested, however, that the summary way in which Bennett and Thompson dispose of Haber's idea of over-voltage is somewhat less conclusive, in view of some of the facts set forth here. They say "Haber assumed that the electrode adsorbs a film of gas and that the resistance is increased. This is not worthy of consideration when it is realized that a resistance at the elec-

trode would lower the electromotive force of the polarized cell," etc.

Now it is clear that the zinc electrode, which has normally a fairly high over-voltage, *does* adsorb a film of gas and that the resistance *is* increased. This notion of Haber's is therefore worthy of some slight consideration. Such consideration will show that the objection that the electromotive force of the polarized cell would be lowered by such a resistance is not insurmountable.

We have seen that the resistance within certain limits of current density may be intermittent in character, that is may be lessened or destroyed during the process of electrolysis, only to reappear when the system is at rest. Such an intermittent resistance would in its effects come within the scope of Bennett and Thompson's definition, that is, that "the term over-voltage * * * will denote the excess back electromotive force of the system under investigation, over the electromotive force of the system consisting of the final product obtained. * * *"

This excess back electromotive force could quite possibly be due in some cases to an intermittent resistance having a low value during active electrolysis and a high value when the system had come to rest in equilibrium with the electrolyte.

That is we might expect a higher E. M. F. with an active system (*i. e.,* in the course of electrolysis), and a lower *apparent* E. M. F. for the final or stable system, the lower E. M. F. being the direct result of the high resistance.

The possibility of some such condition is shown by the following observation. The apparent voltage of a zinc electrode against a neutral electrode rises by several hundredths of a volt upon destroying the contact resistance by passing a sufficiently high current through it, the rise in voltage being that calculated from the observed resistance changes in the electrode. This effect may be observed with an ordinary dry cell. If discharged upon a resistance of 64 ohms, for example, the working closed circuit voltage will shortly be about 0.02 of a volt above the initial open circuit voltage of the cell, due solely to the drop in the contact resistance at the zinc electrode, caused by the current flowing. If the external resistance is greatly increased this rise in working voltage over the initial voltage is diminished, and

finally disappears when the current density becomes too small to affect the stability of the gas film. This provides a possible explanation of the lower voltage of a stable system as compared with an active system, upon the basis of resistance alone. Since the existence of any resistance whatever either for the direct or the reverse reaction, introduces irreversibility to that extent, this factor might be included in any general definition of over-voltage. The over-voltage might be defined as the sum of both the resistance and polarization losses when the current passes to and from the electrode, in a complete electrochemical cycle. That is, it would be the measure of the irreversibility of such a complete reaction cycle. Such a definition would include the resistance losses, if any, incident to the reaction, whereas Bennett and Thompson's definition would ignore irreversibility due to resistance and consider only the polarization loss in the reversal of the reaction.

If resistance phenomena were the sole or major factor in over-voltage, we would expect over-voltage and contact resistance to behave similarly with changes in current density, etc. No such general parallelism seems to exist. In fact electrodes exist which have no appreciable contact resistance and yet have a high over-voltage. In such cases the resistance factor must be completely absent.

In general the treatment of the over-voltage question by Bennett and Thompson is very attractive and the present contention is not that their treatment is in error, but that the exclusion under all circumstances of supplementary factors, and more specifically that of the possible rôle played by resistance is not justified by the present state of our knowledge.

As stated earlier in the paper, more complete data upon various metal electrodes are desirable before making extensive application of these results to over-voltage questions. Perhaps, however, in view of the attention which Prof. Bancroft and Dr. Bennett are directing to the subject of monatomic hydrogen, and with the moral support derived from their papers,[3] I may venture my own speculations as to the nature of the hydrogen equilibria

[3] Bennett and Thompson: Trans. Am. Electrochemical Soc., **29**, 269 (1916). Bancroft: Trans. Am. Electrochemical Soc., **29**, 301 (1916).

on those metal electrodes. The justification for these speculations at this time is that they offer a plausible explanation of the distinctive differences in the behavior of these electrode surfaces, and harmonize well with the general views expressed by the papers referred to.

The plausibility of what follows is particularly dependent upon Bennett's[4] suggestion as to the possibilities of stabilizing—through absorption—certain unstable and otherwise transient intermediates.

My suggestions are these:

(1) That low contact resistance and high over-voltage is evidence that the hydrogen upon the electrode is present principally in the monatomic state. That is, the reaction, $2H \rightarrow H_2$, is extremely slow because of the stabilizing influence of the electrode surface upon atomic hydrogen.

(2) That high over-voltage and high contact resistance is evidence that the hydrogen is present mainly in the molecular state as a heavy film.

That is, the reaction, $2H \rightarrow H_2$ is accelerated, and the surface of the electrode is of such character that the removal of this molecular film in the form of free gas bubbles is exceedingly difficult.

(3) That low over-voltage and low contact resistance indicates the existence of hydrogen mainly in the molecular condition, but in very thin films. That is, the reaction $2H \rightarrow H_2$ is accelerated, but the resulting molecular hydrogen is rapidly discharged as free gas bubbles upon roughened eminences or nuclei afforded by the character of the electrode surface.

Now what do these speculations explain?

First, imagine a metal surface with the desired property of stabilizing monatomic hydrogen, the reaction $2H \rightarrow H_2$ being greatly retarded. We would expect the following consequences:

(a) The concentration of monatomic hydrogen H from the discharge of hydrogen ions would become relatively high. The equilibrium concentration with respect to molecular hydrogen H_2 would be greatly exceeded, resulting as Bennett has shown in high over-voltage.

[4] Bennett and Burnham: Trans. Am. Electrochem. Soc., 29, 217 (1916).

(b) The contact resistance would become very low. The reversible reaction (hydrogen atom $\rightleftarrows$ hydrogen ion), would be facilitated by the high concentration of adsorbed atomic hydrogen in perfect electrical contact with the metal surface, and this reaction would afford a direct and ready means for the transfer of electrical current between electrode and electrolyte, that is it would offer a low resistance path.

(c) Such a high concentration of adsorbed hydrogen would furnish great electrochemical protection to the metal, since the latter could not go into solution without discharging more hydrogen ions which discharge would be directly opposed by the solution pressure of the high concentration of atomic hydrogen already discharged.

In a word our imaginary electrode with its stabilized monatomic hydrogen should be characterized by high over-voltage, extremely low contact resistance, and but slight tendency to local action.

Electrodes having exactly these properties have been experimentally realized.

Second, now suppose the metal surface accelerates the reaction $2H \rightarrow H_2$, giving a high concentration of molecular hydrogen. Two things may result, depending solely upon the character of the electrode surface.

(a) If the metal surface is smooth and the molecular hydrogen film adheres to it, then the film will simply get thicker and thicker until it forms a partial barrier or protective layer between electrode and electrolyte. This layer will introduce high contact resistance between electrode and electrolyte, and hence irreversibility or apparent high over-voltage. In the first case above we had over-voltage due solely to irreversibility arising from unbalanced equilibria. In this case we have over-voltage due to irreversibility arising from the presence of resistance.

The high resistance we may imagine as due either to the physical insulation caused by the film, or as due to the fact that molecular hydrogen cannot be in direct equilibrium with ionic hydrogen but must first undergo an intermediate dissociation into atomic hydrogen. Hence a direct electrical transfer between the molecular hydrogen film and hydrogen ions in solution cannot

take place. In brief, a smooth electrode which accelerates the formation of molecular hydrogen, will show high contact resistance and high over-voltage, and fairly small local action, the latter being determined by the rate of diffusion of the protective gas film. Such an electrode is realized by smooth fresh sheet zinc.

(b) On the other hand, if we suppose that the electrode surface not only accelerates the formation of molecular hydrogen but affords convenient nuclei on its surface for the formation of free gas bubbles, then the presence of these discharging points will keep the film of molecular hydrogen very thin.[5] The result will therefore be that which we find with a zinc surface corroded or roughened with acid, *i. e.,* lowered contact resistance, lowered over-voltage, and no protection against local action.

To summarize: a simple assumption as to the *rate* of the reaction (atomic hydrogen $\rightleftarrows$ molecular hydrogen) enables us to predict three combinations of conditions as to over-voltage, contact resistance and tendency to local action, which have been experimentally observed.

1st. If the reaction, $2H \rightharpoonup H_2$, is very slow, the electrode will exhibit low contact resistance, high over-voltage and great inertness with respect to local action.

2d. If the reaction, $2H \rightharpoonup H_2$, is very rapid, then

(a) Smooth electrodes to which the hydrogen adheres will exhibit high contact resistance, high over-voltage, and considerable inertness with respect to local action.

(b) Roughened electrodes which have points or nuclei upon which gas bubbles may be freely developed, will exhibit low contact resistance, low over-voltage and high local action.

SUMMARY.

1. An explanation of the high contact resistance observed between the zinc electrode and the electrolyte is based upon the supposed existence of a hydrogen film upon the electrode surface, discharged there by local action between the zinc and the electrolyte. This is supported by a considerable amount of experimental evidence, in which it is shown that the predicted behaviour of such

[5] If a smooth metal surface could exist upon which the hydrogen film did not adhere or which it did not "wet" the result would be the same as that for a roughened surface, since the film would break up and form aggregates like oil upon water, leaving certain parts of the metal surface always exposed.

a hydrogen film under selected conditions is in agreement with the observed behavior of the contact resistance.

2. These facts must have a significant relation to the theories of over-voltage phenomena and kindred problems bearing on the nature of the equilibria between the electrode surfaces and the electrolyte.

The writer is indebted to Mr. D. L. Ordway and Mr. C. A. Gillingham for their suggestions during the course of the work.

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DISCUSSION.

President Addicks: I want to read a sentence that I wrote in a discussion in 1905, for these Transactions, about somewhat similar effects in copper. "It is well known that addition agents, such as gelatin, have a perfectly tremendous effect on voltage. A small overdose of gelatin will send the voltage up 40 percent, which would seem to indicate there is a gas film formed there." This is similar to the phenomenon taken up in the paper.

W. R. Mott: This paper is really a consideration of the subject of the *voltage inefficiency* of an electrolytic cell. This voltage loss is made up of two factors: resistance drop at the electrode surfaces (due to gas-films and other insulating products, and to dilution of the electrolyte near the electrodes by withdrawal of chemicals) and overvoltage due to energy lost in the formation and breaking up of intermediate unstable products. To measure the total losses, Dr. J. W. Richards (Trans. Am. Electrochemical Soc. (1904) **5**, 109) made some interesting experiments with an electrolytic cell in a calorimeter. Both losses are equally important. The question arises how these losses can be separated, since measuring the discharge of a cell with a rapidly rotating switch involves in many cases an error increasing with increased speed of rotation, due to capacity effects. If an aluminum anode

and cathode are subjected to 220 volts *direct* current it is easily possible to get (with a suitable electrolyte) a discharge voltage of 150 to 180 volts. Should this be called overvoltage? If an ordinary condenser and resistance are connected in parallel and a rotating switch is arranged for discharge voltage, then the more rapid the rotation the closer will be the discharge voltage to the impressed voltage. The question then is how to distinguish between electrolytic potential of chemical products and that due to dielectric capacity of thin films; since this introduces serious errors into the measurement of overvoltage. One way would be to observe the weight of the electrolytic material in relation to Faraday's law and to obtain its characteristic time-voltage discharge curve, which generally tends to be only slightly dropping, while the condenser effect has a characteristic rapid dropping curve.

C. McC. Gordon: I do not think it is sufficiently realized by most people that almost every metallic electrode you put into a solution has a capacity effect, a real electrostatic capacity, indicating a poorly conducting film. This is especially noticeable in dry cells. If one tries to measure their resistance by an alternating-current bridge, the capacity shows up very clearly. Whether the film be gas or solid is unknown, but almost all electrodes show these capacity effects. The resistance of these films varies with the metal and with the solution, in many cases being so small as to almost mask the capacity effect.

C. W. Bennett: I have no doubt that the rotating commutator does not give the true values of overvoltage, but in our present state of knowledge I do not see but that it is the best thing we have. It does not always give the effect of an increased voltage with an increase of the applied voltage. We do not know by measuring in this way how the overvoltage will decrease with an increase in the charging voltage after a certain point, so that it does give as near the value as any method we know of at the present time. This indicates that the voltage with which the charge is being made is not the all-important factor.

With reference to the paper just presented, I think that we have tried to differentiate between resistance effects and true overvoltage effects, and it is for that reason that measurements of

overvoltage with rotating commutators are considered rather than measurements of the drop of voltage across the cell.

There is another objection, concerning the treatment as a gas electrode. Almost any electrode at certain points may be considered as a gas electrode, but we must deal with overvoltage at points below which the electrodes can be considered as gas electrodes.

The surface tension effect certainly is not all important in determining overvoltage, because we have to deal not only with overvoltage of gases but overvoltage of metals.

Processes carried on electrolytically, the process taking place in two stages, cannot be considered as reversible, and must therefore show overvoltage. Besides this there is the resistance effect, which occurs when any process is carried out at appreciable speed.

The Langmuir theory of overvoltage is that the surface of the metal is covered with hydrogen atoms in such a relation that other hydrogen atoms can combine with them only with difficulty. It appears to me that this is of very little value, because all you have to do is postulate that certain metals have certain properties, and having done so, that is as far as you can go. You cannot use the theory for anything I know of, and the whole thing would, therefore, be valueless.

Some one asked about the carbons that were used in the generation of the ultra-violet light. These carbons were purchased from the Macbeth Printing Lamp Company, and used in the Macbeth printing lamp. It is a flame-arc carbon, and the arc is very nearly white to look at it. There is quite a little ozone generated by the arc, because when the arc is running you can smell the ozone in the air. The carbons are made especially for these 1½ kilowatt printing lamps.

As to the size of the lamp, I measured this once, and took the drop across the carbons. You probably consider the drop across the line. It is a kilowatt and a half across the carbons; I referred to it in my previous paper before the Society.

N. K. Chaney: I wish to call attention to the fact that on page 330 of the advance copy, in the middle of the page, there is a mechanical explanation of the low contact resistance of "corroded" zinc electrodes, as compared with smooth electrodes. For

reasons which cannot be dealt with fully here this explanation is clearly untenable. It was introduced for the sake of developing discussion and is omitted in the final paper.

Mr. Bennett's paper is discussed in the latter part of my own. With reference to this, Mr. Bennett says that overvoltage as he has defined it is "true overvoltage" and that overvoltage phenomena which arise from resistance effects, capacity effects, etc., is "false overvoltage." This is merely a matter of definition and Mr. Bennett is entitled to his own terminology so long as the reality of the phenomena is recognized. If it is admitted that overvoltage effects can arise from irreversibility due to resistance as well as to unbalanced equilibria, and also as Mr. Mott has shown from capacity effects, these facts should be kept clearly in mind. To distinguish between them by the terms "true" and "false" overvoltage is admissable, if generally accepted.

N. K. CHANEY (*Communicated*): The important point to remember is that most overvoltage measurements, including the data in Dr. Bennett's tables are not free from the suspicion of containing these resistance and capacity factors, which Dr. Bennett excludes from his definition of "true" overvoltage. I have pointed out that I am in entire sympathy with Dr. Bennett's general thesis that overvoltage arises largely from unbalanced chemical equilibria of unstable intermediate forms (such as monatomic hydrogen). Disagreement arises only if it is insisted that all other factors are negligible under all conditions and may be safely ignored both in defining the subject and in considering experimental data.

Dr. Bennett further remarks that "we must deal with overvoltage at points below which the electrodes can be considered as gas electrodes," which he regards as "another objection concerning the treatment as gas electrode." Just what this means is not clear. My own paper indicates that there is no point at which an electrode, acting as a gas electrode, ceases so to act with the exception of soluble electrodes at very high current densities.

Dr. Gordon's reference to the very general existence of capacity effects upon metal electrodes of all kinds is in agreement with evidence given in this paper that abnormal resistances due to hydrogen films occur with metals other than zinc, the character-

istics of the resistances vary widely with the metal employed. The large capacity effect in dry cells from this cause makes the bridge method of determining their resistance valueless, as has been brought out previously by Dr. Northrup (Electrical Measurements). For this reason the resistance measurements in this paper were carried out by a direct-current method, which eliminates the capacity factor.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

ELECTRODE SURFACE PHENOMENA.

By William C. Arsem.

In a paper entitled "A Theory of Valency and Molecular Structure" (Jour. Am. Chem. Soc. (1914) **36**, 1655, I outlined a theory of the mode of union of atoms to form molecules, and applied it to the explanation of various phenomena, among which were the formation of ions, and the behavior of electrolytes on the passage of a current. I wish now to show how some of the surface phenomena at electrodes may be explained by this theory.

The theory states that if an atom be considered to be a system of electrons, a molecule is a union of two or more systems in such a manner that one or more electrons is common to each pair of adjoining atoms. If only one electron is shared by two atoms, the union between them is monovalent and can be represented by a single bond. If two electrons are shared, the union is bivalent, and so on. If a molecule is separated at any union in such a way that the shared electrons are divided unequally between the two portions, these portions become ions with electric charges. These ideas were illustrated diagrammatically in the paper referred to above.

It will be seen that a positive ion by gaining an electron would become reversed in sign and be changed into a negative ion, and *vice versa*. The possibility of this reversal seems to me to afford a way of explaining some electrode phenomena.

Let us consider an electrolyte in solution, with a voltage applied between two electrodes, and give our attention to the cathode. Here we have a stream of positive ions approaching the cathode, and in the cathode itself a supply of electrons, tending to escape into the solution. Every positive ion that reaches the cathode or its immediate vicinity will acquire an electron, and become reversed in sign, then as a negative ion it will start on a return

journey toward the anode. Before long, however, it will begin to collide with positive ions approaching the cathode, and eventually one of these collisions will result in union to form a neutral molecule. At a small distance from the cathode there will be a zone where neutral molecules are being formed by collision of ions. We may call this the "neutralization zone" or "collision zone."

Taking, as a concrete case, a cell containing hydrochloric acid being electrolyzed with insoluble electrodes, we would have on the cathode a layer of *negative* hydrogen ions and at some distance away a zone of combination where molecular hydrogen is being formed; and at the anode a layer of *positive* chlorine ions with a corresponding zone of formation of molecular chlorine.

The neutralization zone at the cathode would consist of a saturated water solution of hydrogen but no chlorine or hydrochloric acid. At the anode, if chlorine were the only product of electrolysis we should have in the neutralization zone a saturated solution of chlorine. It is in the neutralization zone that neutral molecules are formed from the ions and afterward deposited on the electrodes. The molecules when first formed are separate or dispersed, that is, they are in the form of a solution.

The neutralization zone, then, is a very thin space close to the electrode surface containing pure solvent, dissolved neutral molecules, and any non-electrolyte which may be present.

As soon as an E. M. F. is applied to a simple cell of this kind, the neutralization zone with its two charge layers of ions begins to form. If the E. M. F. is not too high, a condition of equilibrium is soon reached in which the neutralization zone has a definite thickness and is saturated with the ionic reaction product in molecular form, but contains no ions.

If the E. M. F. is raised above the decomposition point, there is a leakage of ions across the zone, and a further formation of neutral molecules, which are at once liberated since the solution in the zone is already saturated with them. Under these conditions, then, a continuous formation of a molecular product takes place. If the molecular product is normally a gas it collects into bubbles and escapes, leaving enough behind to saturate the solution. If the molecular product is a solid it may condense and

deposit on the electrode as a coherent coating, or it may form fine particles which deposit as a spongy coating or remain disseminated in the liquid, producing in the latter case a "metal fog," such as is sometimes observed in the electrolysis of fused salts.

A solid formed by an ionic reaction in the neutralization zone may be considered as separating from a saturated water solution. It would therefore be expected in some cases to show crystalline properties. Metallic deposits are generally crystalline, and are to be considered as having crystallized out of the solution in the cathodic neutralization zone. The effect of a colloid in the electrolyte would be explained according to this theory as due to interference with crystallization from the water solution, since the colloid would be present in the neutralization zone as well as in the rest of the electrolyte, because it is undissociated.

In cases where the electrode sends ions of its own material into the electrolyte, the product of the ionic reaction in the neutralization zone between the positive ions from the anode and the anions of the electrolyte may be a substance having special properties. When aluminum is used as an anode in some solutions, a very tough film of alumina is formed in the neutralization zone, which under certain conditions of temperature and voltage has been found to be crystalline. S. R. Cook, Phys. Rev. (1905), **26**, 312.

Capacity Effect.

The neutralization zone with its layers of ions of opposite signs on its two faces, constitutes a condenser in which the di-electric is a saturated solution of the product of ionic reaction in the zone, mingled with the product itself, if the latter is a solid. If the product is hydrogen, or a metal, its saturated solution will be very dilute and practically equivalent, as a di-electric, to the pure solvent. The neutralization zone, as a condenser, can be charged to a potential difference, depending on its thickness and di-electric constant and the surface density of the ionic charges on its faces.

The surface density of the charges is, however, limited by the leakage of ions in both directions into and across the zone, and the potential difference will be limited to the breakdown voltage or di-electric strength of the zone.

S. R. Cook (*loc. cit.*) measured the counter E. M. F. of a cell

containing an aluminum anode, and found it practically equal to the E. M. F. used for forming the alumina film. He supposes that the film produces a condenser effect.

Overvoltage.

To maintain a constant flow of ions across the neutralization zone, an E. M. F. higher than its breakdown voltage must be applied and maintained at a value giving the desired rate of leakage of ions. The actual voltage required, over what would be needed if the zone had zero thickness, depends upon the relations between all the factors involved, such as time, temperature, nature of the electrode, condition of the electrode surface, etc. If during electrolysis the cell is disconnected from the circuit and connected to an electrometer, it will momentarily show a back electromotive force equal to the sum of the condenser charges at the anode and cathode neutralization zones.

The maximum decomposition voltage is not reached instantly when an E. M. F. is applied, because time is required to build up the neutralization zone and the charges on its faces.

The variation of overvoltage of hydrogen at cathodes of different metals can be explained thus: If the surface of the cathode is smooth, or has no affinity for hydrogen, there will be no penetration of the positive hydrogen ions before reversal, and there will be a distinct neutralization zone, with a high overvoltage effect.

If the surface of the cathode is rough, or porous, or has a great affinity for hydrogen, there will be penetration of positive ions below the surface of the metal before reversal, and consequently the neutralization zone will be very irregular in shape, or will be absent, because the ionic reaction will take place in the pores of the metal. The overvoltage here would be small.

The first class would include mercury and polished metals, in the second class would come nickel and platinized platinum.

The Nascent State.

It is very probable that reversed ions are extremely active chemically. The strong reducing action at the cathode, for example, may be due to the extraordinary reactivity of the negative hydrogen ion.

The positive hydrogen ion can not have much reducing power, because reduction does not take place in electrolysis except at the surface of the cathode, although positive hydrogen ions are in excess for some distance away from the cathode outside the neutralization zone. The reducing properties of hydrogen in the "nascent state" may also be due to the reactivity of the negative ion, as, when hydrogen is set free in a chemical reaction, half of the atoms before combination to form molecules must be negative, according to the theory of valency referred to above.

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DISCUSSION.

C. McC. Gordon: At the beginning of the third paragraph the paper says: "It will be seen that a positive ion by gaining an electron would be reversed in sign and be changed into a negative ion." The prevalent idea is that when a monovalent positive ion receives an electron it becomes neutral. May I ask Mr. Arsem for an explanation?

William C. Arsem: It would, according to the ordinary theory, but by an example I can indicate what I mean. Suppose a molecule of hydrogen has twenty-one electrons, the only way to split it up would be to have ten on one side and eleven on the other. The side with eleven would be negative and the side with ten would be positive. If we took one off the negative side with eleven and gave it to the side which has ten, it would make that side negative.

C. McC. Gordon: What would be a neutral atom?

William C. Arsem: You could not have a neutral atom unless, instead of one electron being common to both atoms for each bond, you have a group of electrons. In my paper I specifically stated that I would not insist on a single electron. A paper has

just been written by Dr. G. N. Lewis, of the University of California, which is developed along somewhat similar lines. He assumes that two electrons form each bond and has worked out the theory in some detail on that assumption. If it were true that we could divide a molecule of a monovalent element so as to get neutral atoms or uncharged atoms, the theory would have to be modified by assuming that an even number of electrons is common to each pair of adjoining atoms, or that every single bond is made up of an even number of electrons.

N. K. Chaney (*Communicated*): Mr. Arsem's paper deals with certain questions which have been agitating the minds of chemists since the time of Berzelius. The great electrochemical or dualistic system of Berzelius succumbed to the substitution theories of the followers of Dumas and Laurent. You will recall that the rock upon which dualism foundered was the fact that a supposedly electro-positive element, such as the hydrogen in the methyl group of acetic acid, was apparently interchangeable with and replaceable by an electro-negative element, chlorine, in forming trichlor-acetic acid. Had Berzelius suspected the versatility of the hydrogen atom, its capacity for a Dr. Jekyl-to-Mr. Hyde transformation from electro-positive to electro-negative by the swallowing of a solitary electron, his heroic struggle would not have been in vain. Adequately armed with electro-positive and electro-negative varieties of all the elements he could have defied the utmost machinations of the substitutionists.

The outstanding chemical feature of Mr. Arsem's theory is the fact that according to it the existence of a neutral hydrogen atom is a physical impossibility. The dissociation of the hydrogen molecule is always and necessarily an ionic dissociation into positive and negative ions.

$$H_2 \rightleftarrows H^+ + H^-$$

rather than an equilibrium between hydrogen molecules and neutral hydrogen atoms

$$H_2 \rightleftarrows 2H$$

as assumed, for example, in the preceding papers of Dr. Bennett and Prof. Bancroft.

It must be admitted that the conception of this dual nature of the elementary atoms fills a long-felt want in the inorganic as well as in the organic field, whenever we attempt an electro-mechanical explanation of chemical behavior.

In the inorganic field it simplifies the explanation of the formation of molecular doublets by so many of the elements. It seems perfectly natural for an electro-positive and an electro-negative hydrogen atom to combine to form a stable neutral molecule, but it is less obvious why two perfectly neutral atoms, if such can exist, should do the same thing. The right of neutrals to do nothing is the only right which can consistently be permitted them.

The most interesting part of a suggestive and original theory such as this of Mr. Arsem is the number of its corollaries which are susceptible of experimental test.

For example, the solution of molecular hydrogen in palladium, if dissociation occurs at all, must give rise to positive and negative hydrogen ions. If we pass a current through this electrolyte of palladium saturated with hydrogen, there should be a migration of those charged hydrogen ions in opposite directions.

If the palladium is in the form of a wire then the hydrogen should become concentrated at either end of the wire as neutral hydrogen, since the hydrogen ions arriving at each electrode, according to Mr. Arsem, would be met by the oppositely charged (*i. e.,* discharged) hydrogen ions and would neutralize one another in the "collision zone."

Hence by cutting this palladium wire in three pieces after prolonged electrolysis the hydrogen concentration should be found to be high in the end pieces and low in the middle one.

Again, the dissociated hydrogen formed by the hot metal filament in Dr. Langmuir's experiments must consist of positive and negative hydrogen ions which could be separated and concentrated by suitable electrical fields. The two varieties of monatomic hydrogen thus separated should be perfectly stable, since the electro-positive ions, for example, would be unable to combine among themselves.

This separation of electro-positive and electro-negative hydrogen ions should enable us to construct an absolutely dry "dry cell," *i. e.,* a primary battery without any electrolyte whatever.

It would only be necessary to absorb the two kinds of hydrogen ions upon separate battery plates of palladium, and connect the two plates metallically to obtain a current. The reaction would consist in the passage of the electrons of half of the negative hydrogen ions over to half of the positive hydrogen ions, and the resulting mixture of negative and positive ions at each plate would then combine to form molecular hydrogen. This would be strictly an irreversible primary battery. Such a cell, if possible, could not be re-charged simply by reversing the current, since the reversed polarity of discharged ions would cause continuous neutralization in the "collision zone," and so no permanent separation of positive and negative hydrogen by electrolysis could be expected.

As we have indicated, there can be no neutral atoms of monovalent, trivalent, or any odd-valent elements. The even-valent elements, di-valent, quadra-valent and hexa-valent, might however exist as neutral atoms, since they could divide the movable electrons evenly between them upon dissociation. Hence this theory would suggest that fundamental differences might exist between the even and odd valent elements when in the monatomic state. So far as I am aware nothing of the kind has been actually observed.

There are some other questions which must be answered.

Why should the dissociation constant of molecular hydrogen always be zero if both ions are capable of existence in solution on either side of a "collision zone"? We ought to find conditions under which hydrogen could separate at both poles. We ought to be able to find evidence of the migrations of negative sodium atoms and positive chlorine atoms somewhere outside of the restricted boundaries of the "collision zone." Failing in this, many of us will be inclined to suspect that the difficulties introduced by this particular theory are scarcely outweighed by its advantages.

William C. Arsem (*Communicated*): As Mr. Chaney says, the theory suggests a number of interesting corollaries, which might be submitted to test, and I hope somebody will be interested enough to try experiments along these lines.

I wish to point out once more that even if neutral monatomic hydrogen exists, my theory of valency would not be rendered

invalid. It would, for example, be quite natural to assume that a bond consists of two electrons revolving about the axis joining the positive nuclei as in Bohr's hydrogen molecule, and that this pair of electrons or "valency ring" can, under some conditions, be divided so that one electron of the pair revolves about each nucleus. This would give two neutral atoms, whereas if the "valency ring" goes with one nucleus when dissociation takes place, both atoms will be charged.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

THE PASSIVE STATE OF METALS.

By C. W. Bennett and W. S. Burnham.

The phenomenon of passivity was probably first noted with iron,[1] when treated with concentrated nitric acid. The general property has later been found marked in the cases of aluminum, chromium, nickel, tin, and cobalt. Passivity[2] is also found in the cases of tungsten, molybdenum, silver, bismuth, platinum, zinc, magnesium, aluminum, copper, lead, columbium, vanadium, ruthenium, gold, tantalum, uranium, manganese, and to some extent probably with most of the metals under extreme conditions. Attempted explanations of the facts of passivity have dealt largely with iron, consequently in this discussion iron will be studied more in detail than other cases of passivity. The other metals will be considered, however.

The passive state of iron is a condition which it acquires when it is exposed to the action of oxidizing agents, whereby its surface becomes more noble, in other words its solubility is decreased. The single potential is a noble one, rather than the less noble one associated with iron itself. The measurement of this potential has been used to test the presence of the passive state.[3] It has led to many contradictions, however, on account of the fact that different solutions are used and different values obtained. Furthermore, too much depends on the method of meas-

[1] Keir: Phil. Trans. (orig.), **80**, 359 (1790); Abridged by Hutton, Shaw and Pearson (1809), **16**, 694 (1785-1790).

[2] See Dunstan and Hill: Jour. Chem. Soc., **99**, 1853 (1911).

[3] Keir: *l. c.*
Wetzlar: Schweigger's Jour. Chem. u. Phys., **56**, 206 (1829).
Fechner: *Ibid.*, **53**, 61, 129, 151 (1828).
Joule: Phil. Mag. (3) **24**, 106 (1844).
Beetz: Pogg. Ann., **67**, 286, 365 (1846).
Corsepius: Beiblätter (Wied. Ann.), **11**, 272 (1887).
Dissertation, Munich, 1886.
Martens: Mem. de l' Academie de Bruxelles, **19**, 3 (1845).
Hittorf: Zeit. phys. Chem., **34**, 385 (1900).
Michell: Arch. des Sci. phys. et nat. (4) **10**, 122 (1900).
Finkelstein: Zeit. phys. Chem., **39**, 91 (1902).
Fredenhagen: Zeit. phys. Chem., **43**, 1 (1903).
Muthmann and Frauenberger: Sitzungber der Kgl. Bayrischen Akad., **34**, 210 (1904).

urement. The non-replacement of copper or silver ions has also been used.[4] The use of nitric acid of such strength that passive iron when placed therein remains passive but in which active iron dissolves readily,[5] is the most satisfactory criterion of passivity. For the sake of uniformity, since there are degrees of passivity, we may take Heathcote's test for the passive state of iron.[6] He employed nitric acid, testing the chemical action. "The rod was regarded as passive when after plunging in 1.2 nitric acid, and shaking for a moment in the acid and then holding motionless, no chemical action could be detected at the surface by the unaided eye, the temperature of the acid being about 15°-17° C." The nitric acid referred to above is 1.20 specific gravity.

A number of investigations have been made on passive iron, and the reaction has been considered from a number of viewpoints. Keir[7] noted that only strong nitric acid rendered iron passive, and that when passive iron was scratched, or brought in contact with active metal, it became active.

These experiments seem to have been lost sight of, and the facts were rediscovered by Wetzlar.[8] The position of passive iron in the electrochemical series was determined by Fechner.[9]

[4] Wetzlar: Schweigger's Jour. Chem. u. Phys., **49**, 470 (1827).
Fischer: Pogg. Ann., **6**, 42 (1826).
Wöhler: *Ibid.*, **85**, 448 (1852).
Senderens: Bull. Soc. Chim., **15**, 691 (1896); **17**, 279 (1897).
de Brenneville: Jour. Iron and Steel Inst., **52**, 40 (1897).

[5] Herschel: Ann. Chim. Phys. (2) **54**, 87 (1833).
Schönbein: Pogg. Ann., **37**, 390, 590 (1836).
Mousson: *Ibid.*, **39**, 330 (1836); Bibl. Univ. de Genève (Sept., p. 165 (1836).
Faraday: Phil. Mag. (3) **9**, 53, 122 (1836).
Noad: *Ibid.* (3) **10**, 276 (1837); (3) **12**, 48 (1838).
Herschel: *Ibid.* (3) **11**, 329 (1837).
Renard: Comptes rendus, **79**, 159, 508 (1874).
de Regnon: *Ibid.*, **79**, 299 (1874).
Varenne: *Ibid.*, **89**, 783 (1879); **90**, 998 (1880).
Nichols: Amer. Jour. Science (3) **31**, 272 (1886).
Nichols and Franklin: *Ibid.* (3) **34**, 419 (1889).
Belck: Dissertation, Halle, A. S. (1888).
Gautier and Charpy: Comptes rendus, **112**, 1451 (1891).
Andrews: Proc. Roy. Soc. (London), **49**, 120 (1891).

[6] Heathcote: Jour. Soc. Chem. Ind., **26**, 899 (1907).

I should state here that the freest use has been made of the excellent bibliography in this article, as well as that in Byers' paper noted below.

[7] Phil. Trans., *l. c.*

Bergman it seems also noted that iron did not dissolve in silver nitrate solution. Phil. Trans. (orig.) 80, 374 (1790). Abridged by H, S, and P (1809), **16**, 703 (1785-1790).

[8] Wetzlar: Schweigger's Jour. Chem. u. Phys., **49**, 470 (1827); **50**, 88, 129 (1827); **54**, 324 (1828); **56**, 206 (1829); **58**, 302 (1830).
See also Broconnot: Ann. Chim. Phys. (2) **52**, 288 (1833); Pogg. Ann., **29**, 174 (1833).

[9] Fechner: Schweigger's Jour. Chem. u. Phys., **53**, 129 (1828). See also *Ibid.*, **53**, 151 (1826).
Pogg. Ann., **47**, 1 (1839).

Westlar[10] attributed the inability of iron to replace copper after being placed in silver nitrate, to the assumption of a negative charge by the part immersed.

Herschel[11] published the first results explaining passivity on the basis of electrical phenomena. Publishing in 1833, the results of his work in 1825, he says that "passive [*préparé*] iron may be withdrawn from the acid and exposed to the air, dipped in water or ammonia without regaining activity [*la propriété d'être attaqueé par l'acide nitrique*]. It may be touched lightly in the acid or in the air with gold, silver, platinum, mercury, glass, and many other substances without destroying the passive state. But if the surface be rubbed vigorously, giving intimate contact, for instance; if it is scratched with the edge of a piece of glass, the passive state is destroyed. . . . On the other hand, if passive iron in water, air, or in the acid, be touched with copper, zinc, tin, bismuth, antimony, lead, or active iron, passivity is destroyed. . . . If a long iron wire passivated and moistened with acid is touched with copper at one end, while suspended in air, the surface becomes brown, not instantaneously, and all at once, but by a progressive [*successivement*] movement, spreading, so to speak, from the end touched to the other. . . . Once passivified, iron resists nitric acid of the concentration in which it was passivated, or even more dilute, which shows that these phenomena are due, not to a lack of solvent for the iron salt, but rather to a certain *permanent electrical condition of the surface* of the metal. This viewpoint is strengthened by following experiments. . . .

"A piece of iron wire was coated with wax in the center, so that the piece was divided into two parts. When this wire was put into strong nitric acid, action stopped on each end at the same time; when one end was touched with copper, action started simultaneously on each side. . . . [*when however*] the iron was withdrawn from the acid into the air, and then touched, the action started at the end touched and ran the whole half of the wire,

[10] Ann. des Mines (Third Series) **2**, 322 (1832).

Mag. Pharm., 1830. The references printed in italics have not been checked. These publications were not readily available. The above Westlar is probably the same as Wetzlar, the former being a French misspelling of the German "Wetzlar." This, however, could not be determined with certainty, because the original paper of Westlar (sic) was not available.

[11] Herschel: Ann. Chim. Phys. (2) **54**, 87 (1833).
Pogg. Ann., **32**, 211 (1834).
Phil. Mag. (3) **11**, 329 (1837).

but was stopped by the wax." In this condition, if the wire is dipped into the dilute acid, the whole was observed to become active, although the experiment was performed in a little different way.

Schönbein, who suggested the term passivity, next studied the subject.[12] He found that when a part of an iron rod was passivated, by dipping deeper into the dilute acid a larger surface could be passivated. If two pieces of iron, one active and the other passive, were partly immersed in dilute nitric acid, and then electrically connected outside of the acid, the active rod becomes passive if the immersed surface is not too great. If the surface is much greater than the immersed area of the passive rod, the latter will become active. The combination becomes passive or active depending on the relative areas of the original active and passive rods. It was also found that iron could be passivated when made anode in nitric acid, and that the passive state was destroyed by touching the iron with the negative electrode. With the source of current used, the circuit had to be closed by putting the iron in the acid, otherwise passivity was not produced. When there was set free at the iron surface any substance like chlorine, which has a "strong affinity" for iron, no passivity could be produced. Iron was therefore made passive when anode in nitric acid, sulphuric and phosphoric acids, but could not be made passive under these conditions when chlorides, bromides, fluorides, or iodides were used. He concluded that bismuth[13] could be passivated, but cobalt and nickel could not.

Faraday[14] in answer to a request of Schönbein to explain his results noted that active iron in 1.35 acid was made passive by touching with gold, platinum, or carbon. Oxide films, which are invisible to the naked eye, and also insoluble in nitric acid, are formed by heating iron in air or oxygen. Since such a protec-

[12] Schönbein: Phil. Mag. (3) **9**, 53, 259 (1836); (3) **10**, 133, 172, 267, 425, 428 (1837); (3) **11**, 544 (1837).
Pogg. Ann., **37**, 390, 590 (1836); **38**, 444, 492 (1836); **39**, 137, 342, 351 (1836); **40**, 193, 621 (1837); **41**, 41, 55 (1837); **43**, 1, 13, 89, 103 (1838); **57**, 63 (1842); **59**, 149, 421 (1843).
Bibl. univ. nouv Serie, **9**, 416; **18**, 366.
Arch. de l'Electr., **2**, 269 (1842).

[13] See Andrews: Phil. Mag. (3) **12**, 305 (1838).
Pogg. Ann., **45**, 121 (1838).
Proc. Roy. Soc. (London), **46**, 176 (1889); **48**, 116 (1890); **49**, 481 (1891).
Nature, **43**, 358 (1891).
Beiblätter (Wied. Ann.) **14**, 1144 (1890); **15**, 428 (1891).

[14] Faraday: *Experimental Researches, 8th series, sec.* 947-996 *and Vol.* **2**, 237.
Phil. Mag. (3) **9**, 53, 122 (1836); (3) **10**, 175 (1837).

tion of the metal is possible, and on account of the fact that all passivifying processes are oxidation processes, Faraday concluded, that "the surface of the iron is oxidized, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation. . . .

"The state seems to me to be one of a very delicate equilibrium of forces, though of course that condition of things which can produce it can also retain it; and this notion seems to be confirmed by the intermitting action originally mentioned by Herschel."

Nicklès[15] showed that nickel and cobalt may also be passive. Nichols and Franklin[16] showed that passive iron dissolves slowly in nitric acid. Buff[17] showed that aluminum was passive under a variety of conditions. Beetz[18] reviewed and tested previous work but developed very little otherwise. This is also true of the large volume of the literature published from the time of Faraday's and Schönbein's work,[19] until Hittorf revived interest in passivity by his work on chromium.

A number of solutions besides nitric acid may develop the

[15] Nicklès: Comptes rendus, **37**, 284 (1853).
Pogg. Ann., **90**, 351 (1853).

[16] Nichols and Franklin: *l. c.*

[17] Liebig's Ann., **102**, 265 (1857).

[18] Beetz: Pogg. Ann., **62**, 234 (1844); **63**, 415 (1844); **67**, 186, 365 (1846).
Arch. de l'Electr., **4**, 509, 600.
Rep. der Physik., **8**, 256 (1849).
Pogg. Ann., **127**, 45 (1866).
Wied. Ann., **2**, 94 (1877).
Münch Ber., **1875**, 59.
Pogg. Ann., **156**, 464 (1875).

[19] This list, taken from the several reviews of the subject referred to below, contains references not heretofore given down to the work of Hittorf on chromium (1898).
Kirwan: "On Phlogiston," Precipitation of Metals, p. 244 (1789).
Vanquelin: Scherer's Allg. Jour. Chem., **3**, 331 (1799).
Thenard: Ann. Chim., **56**, 59 (1805).
Sylvester: Gehlen's Jour. Chem. Phys., **1**, 539 (1806).
Davy: Gilbert's Ann., **51**, 206 (1815).
Phil. Trans., **116**, Pts. 2-3, 383 (1826).
Ann. Chim., Phys. (2) **33**, 276 (1826).
Pfaff: Gilbert's Ann., **69**, 84 (1821).
Schweigger's Jour. Chem. u. Phys., **53**, 77 (1828).
Oersted: Ann. Chim. Phys. (1) **22**, 358 (1823).
Avogadro: *Ibid.*, (1) **22**, 361 (1823).
Marianini: Schweigger's Jour. Chem. u. Phys., **49**, 452 (1827).
Ann. Chim. Phys. (2) **45**, 40 (1830).
De la Rive: Ann. Chim. Phys. (2) **36**, 34 (1827).
Pogg. Ann., **10**, 425 (1827).
Arch. de l' Elect., No. **5**, 267.
Schweigger and Siedel: Schweigger's Jour. Chem. u. Phys., **53**, 167 (1828).
Van Beek: Pogg. Ann., **12**, 274 (1828).
Berzelius: Jahrbuch, **8**, 104 (1829).
Daniell: Phil. Trans., **126**, 114 (1836).
Wartmann: Essai historique sur les phénomènes de l'électrochimie (1838).
Maas: Bull. Acad. roy. de Bruxelles, **6**, 2d Pt., 438 (1839).
Chateau and Boutmy: Cosmos, **19**, 117.
Grove: Phil. Mag. (3) **15**, 292 (1839).
Pogg. Ann., **48**, 300 (1839); **49**, 600 (1840); **63**, 424 (1844).
Arch. de l'Electr., **4**, 167.
Martens: Pogg. Ann., **55**, 437, 612 (1842); **61**, 121 (1844); **63**, 412 (1844).
Bull. Acad. roy. de Bruxelles, **7**, 1st Pt., 393 (1840).

passive state of iron without the aid of an external current. Keir passivified iron with a solution of silver nitrate; Kirwan used lead nitrate; Boutmy and Chateau,[20] potassium permanganate and dichromate, chloric acid, and arsenic acid; Schönbein, mercuric nitrate and sulphuric acid to which nitrous acid was added; Wetzlar, copper potassium tartrate and ammoniacal copper solution; while Beetz used chromic acid. Varenne showed that compressed nitric oxide will make iron passive. Young and Hogg[21] have shown that iron when becoming passive may adsorb weighable amounts of nitrogen peroxide, and that on exposure to moist atmosphere this comes out with the formation of drops of acid on the piece of metal. Boutmy and Chateau with Muthmann and Frauenberger have shown that oxygen from the air will develop the passive state of iron. Renard claims that the vapors of strong nitric acid will cause passivity.

Millon: Pogg. Ann., **57**, 289 (1842).
Comptes rendus, **21**, 47 (1845).
Ohm: Pogg. Ann., **63**, 389 (1844).
Phillips: Phil. Mag. (3) **33**, 509 (1848).
Wöhler: Pogg. Ann., **85**, 448 (1852).
Liebig's Ann., **82**, 248 (1852).
Wheatstone: Phil. Mag. (4) **10**, 143 (1855).
Heerer: Mitt. Gewerbver. Hannover, 342 (1855).
Osann: Pogg. Ann., **96**, 498 (1855).
Wöhler and Buff: Liebig's Ann., **103**, 218 (1857).
Kestner: Ann. Chim. Phys. (3) **55**, 330 (1859).
Anon: Jour. prakt. Chem., **83**, 209 (1861).
Heldt: Jour. prakt. Chem., **90**, 257-288 (1863).
St. Edmé: Comptes rendus, **51**, 507 (1860); **52**, 930 (1861); **106**, 1079 (1888); **109**, 304 (1889).
Peretti: (Pamphlet) Dell' Azione chimica dell' Acqua sopra i Soli e Sopra gli Acidi, Rome (1861).
Ordway: Silliman's Am. Jour. Sci. (2) **40**, 316 (1865).
Jour. prakt. Chem., **99**, 366 (1866).
Tomlinson: Proc. Roy. Soc. (London), **16**, 403 (1868); **17**, 240 (1869); **18**, 533 (1870).
Phil. Mag. (4) **34**, 136, 229 (1867).
Trans. Chem. Soc., **22**, 125 (1869).
Cailletet: Comptes rendus, **68**, 395 (1869).
Ducretet: Jour. de Physique, **4**, 84 (1875).
Comptes rendus, **80**, 280 (1875).
Moissan: Comptes rendus, **84**, 1296 (1877); **86**, 600 (1878).
Ramann: Ber., **14**, 1430 (1881).
Bibart: Nature, **24**, 179 (1881).
Oberbeck: Wied. Ann., **19**, 625 (1883).
Laurie: Phil. Mag. (5) **22**, 213 (1886).
Streintz: Wied. Ann., **32**, 116 (1887); **34**, 751 (1888).
Veley: Proc. Roy. Soc. (London), **46**, 216 (1889); **48**, 458 (1890).
Jour. Chem. Soc., Abst., **60**, 525 (1891).
Neumann: Zeit. phys. Chem., **14**, 193 (1894).
Ditte: Comptes rendus, **110**, 573 (1890); **128**, 195 (1899).
Ann. Chim. Phys. (7) **16**, 152 (1898).
Pollak: Comptes rendus, **124**, 1443 (1897).
Gratz: Wied. Ann., **62**, 323 (1897).
Askenasy: Zeit. Elektrochemie, **4**, 70 (1897).
Lecher: Ber. Wein Akad., **107**, 2a, 739 (1898).
Guthe: Phys. Rev., **15**, 327 (1902).
Bredig and Haber: Ber., **31**, 2741 (1898).
Scott: Wied. Ann., **67**, 388 (1899).

[20] Cosmos, **19**, 117.

[21] Young and Hogg: Jour. Phys. Chem., **19**, 617 (1915).
See also Weber: Jour. prakt. Chem., **114**, 342 (1873).

The process is not instantaneous, but a certain time is used to develop the state. This time varies with the conditions of electrolyte, temperature, etc. It is found, however, that the time required for passivity varies inversely with the oxidizing (in a general sense) power of the solution. If the metal be made anode, the time required for passivity varies inversely with the current density, with the exception that at low current densities, iron, for instance, does not go passive at all. With an anode voltage less than 0.65[22] no passivity occurred in sulphuric acid. As anode the metal becomes more noble gradually until finally it reaches practically a stationary state at about — 0.75 volt (absolute) in sulphuric acid. A sample of the metal seldom acts the same in being passivated repeatedly.

The active condition is restored by making the metal cathode or bringing it in contact with the cathode, by stirring or scratching. Keir and Buff noted that passive iron becomes active when placed in water. Noad found that dilute nitric acid destroyed passivity. Schönbein found that either chlorine, bromine, hydrochloric acid, sulphuric acid, or potassium chloride solution restored the active state. This change is just the reverse of the passivifying operation. The metal becomes less noble until finally activity is restored. Considering the voltage-time curve of either process, there is a more or less rapid rise or drop to an intermediate value where the voltage is very nearly constant with time, and then another rather sudden rise or fall of the voltage, and the metal is no longer active or passive as the case may be. Above this nearly constant voltage the metal is always passive while below this, it is always active. Martens claims that passive iron when placed in an activifying solution of copper sulphate becomes coated with a good deposit of copper, very different from that obtained by immersing iron in the copper solution. This shows probably that the activation is a process which exposes the metal surfaces only gradually. Belck and

[22] Heathcote: *l. c.*
For other reviews see
Schönbein: Das Verhalten des Eisens zum Sauerstoff (1837).
Berzelius: Lehrbuch, Vol. II, 629 (1844).
Wiedemann: Lehrbuch der Elektricität, Vol. II, 812 (1894).
Ostwald: Elektrochemie, p. 696 (1896).
Sackur: Chem. Ztg., **28**, 954 (1904).
Fredenhagen: Zeit. phys. Chem., **63**, 1 (1908).
Byers: Jour. Am. Chem. Soc., **30**, 1718 (1908).
Grave: Jahrbuch der Radioaktivität u. Elektronik, **8**, 91 (1911).
Friend: The Corrosion of Iron and Steel, Chap. 12 (*Longmans*, 1911).
Senter: Trans. Faraday Soc., **9**, 203 (1914).

Varenne claim that passive iron becomes active when placed in a vacuum. Heathcote, however, has shown that iron may be kept passive in a vacuum for hours. Spots of activity may occur, however, and some of the samples become active under such influence.

While iron is passive it is really dissolving. Faraday showed that iron as anode in nitric acid dissolves slowly. Heathcote showed that the rate of solution is the following. The current was 0.085 ampere for 18 minutes.

Specific Gravity of Nitric Acid.	Iron Dissolved Gram.
1.40	0.0141
1.30	0.0108
1.15	0.0079

Without the current the indications are that the rate of solution is less the more dilute the acid, although this cannot be said with certainty since there are so many factors that may vary. It is impossible to measure the solubility under such conditions. The phenomenon must, therefore, be considered as dynamic rather than static. In fact Heathcote emphasizes this when he says "the appellation 'passive' is only true so far as the sense of sight is concerned; passive iron is really the seat of a multitude of changes."

This is realized when one considers the pulsation of activity and passivity mentioned by Herschel. In passivifying a piece of iron a surge or pulsatory movement of the zone of passivity back and forth very often occurs. In fact if two strips of iron are connected to a galvanometer and dipped in a passivifying solution, there will be a pulsation of current back and forth. This may be followed on a rod by watching the evolution of gas. When passive iron is touched with a less noble metal a surge back and forth will occur. Pulsations often take place just before passive iron becomes active when placed in dilute nitric acid.

A number of the properties of passive and active iron have been studied in attempts to explain passivity. The reflecting power of the material in the two states has been measured.[23] A piece of iron was polished and made anode and cathode succes-

[23] Müller and Königsberger: Zeit. Elektrochemie, **13**, 659 (1907).
Phys. Zeit., **5**, 413, 797 (1904); **6**, 847 (1905); **7**, 796 (1906).
Beiblätter (Drude's Ann.) **29**, 711 (1905).

sively in a passivifying solution. Oxygen was deposited at the surface as anode and hydrogen at the surface as cathode. No difference in the reflecting power of the anode and cathode was noted, although the method was claimed to be sufficiently accurate to detect a film of oxide, 0.8 $\mu\mu$ thick in the case of lead. This caused these observers to say there could be no *oxide film* present.

Since the above experiment showed negative results in distinguishing by physical means between active and passive iron, some physical properties which show differences may be given. When aluminum is made anode in sulphuric acid, for instance, it is covered with an insoluble film of oxide which contains some gas in its pores. This covering may be considered as a di-electric where the metal and electrolyte form the two conductors. The arrangement may be considered an electro-static condenser[24] which will show "capacity." Passive iron in most cases shows such capacity,[25] while active iron does not. The experimenters conclude that a solid film must be assumed to explain their results.

When a polished metal plate is exposed to ultra-violet light, it readily loses a negative charge, becoming positively charged. A measure of this loss of negative charge is known as the photo-electric effect of the metal. This has been measured and it was found that active iron exhibits a strong photo-electric effect, while passive iron shows much less, and sometimes scarcely a measurable effect.[26] Metals exposed to air show photo-electric fatigue or a decrease in the photo-electric activity. This falls in line with the statements of Muthmann and Frauenberger that atmospheric air may passivify iron. Just as iron may show degrees of passivity, so does it show degrees of photo-electric activity. The phenomena of chemical activity and photo-electric activity of iron vary concomitantly, and have therefore been referred ultimately to the same general cause.

Faraday's explanation of the passivity of iron was more or less accepted, and Wiedemann rather without evidence put down the oxide as Fe_3O_4, which has gradually crept into the text-books and some of the literature on the subject. This view was called in question when the next important case of passivity was studied.

[24] See Schulze: Trans. Faraday Soc., 9, 268 (1914).

[25] Gordon and Clark: Jour. Am. Chem. Soc., 28, 1534 (1906).
Zeit. Elektrochemie, 12, 769 (1906).

[26] Allen: Proc. Roy. Soc. (London), 88 A, 70 (1913).
Trans. Faraday Soc., 9, 247 (1914).

Hittorf[27] showed that when chromium is dipped in oxidizing solutions it becomes passive, and is more noble than silver or mercury. It does not reduce gold, platinum, or palladium chloride even at the boiling temperature. Evidently the solutions were not concentrated. The temperature probably was not much above 100° C. It was found that chromium could be passive or active in the same solution when the chromium was anode, depending on the temperature. Chromium as anode dissolves in zinc chloride solutions at ordinary temperatures as hexavalent ion and the metal is in its noble condition. In other words it is passive. At elevated temperatures under the same conditions otherwise, the chromium is active and dissolves as bivalent metal. In the case of $ZnCl_2$, the temperature has to be 130° C. In this state chromium is less noble than hydrogen.

In an alcoholic solution of zinc chloride Hittorf claims that chromium dissolves as trivalent ion, and the metal occupies an intermediate state in the voltaic series. This has later been shown to be due to experimental error.[28] Some alcohol is oxidized to aldehyde. If this is neglected the valence may range from 2.25 to 11.9, depending on the conditions of temperature and current density. The more alcohol oxidized the higher the apparent valence of the chromium.

Active chromium replaces hydrogen and forms chromium iodide when placed in hydriodic acid, but passive chromium is not affected by hydriodic acid or even as anode in potassium iodide. Furthermore, chromium may be made to assume the passive state when made anode in potassium iodide solution. This was considered as conclusive by Hittorf that the passivity of chromium was not due to an oxide film. He also included iron with nickel and cobalt in this class, since he showed that these metals may assume the passive state. He concludes that passivity is due to a strained or coerced condition (Zwangzustand) of the metal whereby it dissolves with different valences. There is no attempt to determine what causes the change in the metal.

Nickel in air is passive. It will not replace copper from copper

[27] Zeit. phys. Chem., **25**, 729 (1898); **30**, 481 (1899).
Zeit. Elektrochemie, **4**, 482 (1898); **6**, 6 (1899).
Sitzungsberichte Berliner Akademie, Mch. 10 (1898).
General on passivity: Zeit. phys. Chem., **34**, 385 (1900).
Zeit. Elektrochemie, **7**, 168 (1900).

[28] Kuessner: Zeit. Elektrochemie, **16**, 769 (1910).

sulphate. Nickel is passive as anode in sulphuric acid[29] or sulphates, nitrates, and alkalies. Byers claims practically no solution of a passive nickel anode, while Sackur claims that it dissolves slowly. The passivity is hindered by rise in temperature.

Cobalt may be made passive as anode in carbonates, bichromates, oxalates, and alkalies. In sulphates the passivity is periodic and occurs only at high current densities.

Grube[30] has shown that iron, lead, silver, and zinc become passive when made anode in alkaline solutions of potassium ferrocyanide. Anodes of iron, nickel, cobalt, copper, lead, and silver become passive in neutral solutions of potassium ferro-cyanide. He observes that passivity is accompanied by the appearance of a visible film.

Magnesium[31] will become passive anodically and under such conditions dissolves with a valence of nine.

Tin becomes passive in sodium stannate solutions[32] anodically.

The passivity of aluminum, coupled with its "valve action," has been studied closely.[33] The film which is unquestionably present is a non-conducting one, hence it is probably not continuous. A film of gas serves to give the aluminum electrode

[29] Le Blanc and Levi: Boltzmann's Festschrift, p. 183 (1904).
Riesenfeld: Zeit. Elektrochemie, **12**, 621 (1906).
Thiel and Windelschmidt: *Ibid.*, **12**, 737 (1906).
Sackur: *Ibid.*, **14**, 607 (1908).
Byers: Jour. Am. Chem. Soc., **30**, 1741 (1908).
Alvares: Zeit. Elektrochemie, **15**, 142 (1909).
Schoch and Randolph: Jour. Phys. Chem., **14**, 719 (1910).
Schoch: Trans. Faraday Soc., **9**, 274 (1914).

[30] Grube: Trans. Faraday Soc., **9**, 214 (1914).
Zeit. Elektrochemie, **18**, 189 (1912).

[31] Bavorovsky: Zeit. Elektrochemie, **11**, 465 (1905).

[32] Eckardt: Zeit. phys. Chem., **56**, 391 (1906).

[33] Buff: Liebig's Ann., **102**, 265 (1857).
Beetz: Wied. Ann., **2**, 94 (1877).
Pollak: Comptes rendus, **124**, 1443 (1897).
Graetz: Zeit. Elektrochmie, **4**, 67 (1897).
Norden: *Ibid.*, **6**, 155, 188 (1899).
Ditte: Ann. chim. Phys. (7) **16**, 152 (1898).
Comptes rendus, **110**, 573 (1890); **128**, 195 (1899).
Guthe: Phys. Rev., **15**, 327 (1902).
Burgess and Hambeuchen: Trans. Am. Electrochem, Soc., **1**, 147 (1902).
König: Elektrotechn. Zeit., **23**, 474 (1902).
Taylor and Inglis: Phil. Mag. (6) **5**, 301 (1903).
Nodan: Electrochem. Ind., **1**, 222, 284 (1903).
Int. Elect. Cong. (St. Louis) **1**, 510 (1904).
Electrochemist, **3**, 444, 772 (1904).
Fischer: Zeit. Electrochemie, **10**, 869 (1904).
Cook: Phys. Rev., **18**, 23 (1904).
Charters: Jour. Phys. Chem., **9**, 110 (1905).
Zimmerman: Trans. Am. Electrochem. Soc., **5**, 147 (1904); **7**, 309 (1905).
Sebor and Simck: Zeit. Elektrochemie, **13**, 113 (1907).
Bairsto: Trans. Faraday Soc., **8**, 232 (1912).
On the behavior of several metal anodes, see
Schulze: Drude's Ann., **21**, 929 (1906); **22**, 543 (1906); **23**, 226 (1907); **24**, 43 (1907); **25**, 775 (1908).
Zeit. Elektrochemie, **14**, 333 (1908); **18**, 22 (1912).
Trans. Faraday Soc., **9**, 266 (1914).

"capacity."[34] Aluminum is passive in air, and remains so in solutions which do not attack the oxide covering. It is supposed that this film consists[35] of a very thin non-porous layer of oxide, covered by a porous one, with gas occluded in the pores of the outer film. The outer film may slowly dissolve, while the inner one becomes porous and is replaced by a new one formed by the oxygen liberated, breaking through the original film.

Under conditions of high current density, low temperature, and strong sulphuric acid, lead as anode dissolves as tetravalent lead.[36] While we do not know what the potential of the lead is, this is a case of retarded solution, strictly analogous to the passivity of chromium.

A lead anode in dilute sulphuric acid, for instance, becomes covered with lead dioxide, in quantities such that there is no question about the film. The combination is noble, and the film is destroyed by hydrochloric acid. When thus protected by oxide, the lead dissolves only slowly in sulphuric or nitric acid.

Attempts have been made to induce passivity of lead anodically without a visible film.[37] The results were not highly satisfactory, however. One of the experiments with strong nitric acid without the current may be given. A lead rod when dipped in concentrated nitric acid is not so soluble in 25 percent acid as it was before immersion in the former. For instance, two rods suspended in concentrated acid, one for three minutes, the other for one day, showed the following quantities of lead dissolved in 25 percent acid in two hours as compared with a lead rod not treated with strong acid. The surface was the same in all cases. The lead in solution was determined as sulphate.

	Quantity of lead (calc. from sulphate) dissolved in 2 hours.
Rod not treated (blank)	0.7951 gram
Rod treated three minutes	0.7900 "
Rod treated one day	0.4725 "

Thus by treating with strong nitric acid, there is a retardation of the chemical solution of lead in dilute nitric acid.

It has been noted that manganese, or rather ferro-manganese,

[34] Schulze: *l. c.*

[35] Schulze: Drude's Ann., **28**, 789 (1909).

[36] Elbs and Fischer: Zeit. Electrochemie, **7**, 343 (1900).

[37] These experiments were performed for us by Douglass and Wendt.

as anode[38] dissolves with the formation of potassium permanganate, in other words with a valence of seven. The normal reaction of manganese and caustic soda, for instance, involves the formation of manganous hydroxide. When the current density is raised, permanganate is formed. Attempts to oxidize manganous hydroxide and manganese dioxide at the surface of platinum to permanganate have been unsuccessful. It seems here that we have a case of the formation of the higher oxide when metallic manganese is present, but not in its absence. At any rate we have another case of retarded solution, or solution of the metal with a higher valence, than normal. Thus the manganese as well as the lead have been made passive. It is highly probable that the passive state of this metal is so unstable that it persists only under anodic influences and consequently those who have measured potentials of the metals have said that manganese did not exhibit passivity.[39]

Copper when used as anode in sodium hydroxide becomes passive[40] and is coated with a film of Cu_2O_3. Zinc[41] develops the passive state both chemically and anodically, in which condition it becomes more noble.

Tungsten,[42] uranium, tantalum,[43] molybdenum,[44] vanadium,[45] columbium, ruthenium,[46] platinum,[47] gold,[48] bismuth,[49] and cadmium[50] also exhibit the phenomenon of passivity.[51]

[38] Lorenz: Zeit. anorg. Chem., **12**, 393 (1896).
White: Trans. Am. Electrochem. Soc., **9**, 255 (1906).
Kuessner: Zeit. Elektrochemie, **16**, 758 (1910).

[39] Zeit. Elektrochemie, **10**, 929 (1904). See also *Ibid.*, **11**, 755 (1905).

[40] Müller and Spitzer: Zeit. Elektrochemie, **13**, 25 (1907).
Müller: *Ibid.*, **13**, 133 (1907).

[41] Centnerszwer and Drucker: Jour. Chim. phys., **13**, 162 (1915).

[42] Rideal: Trans. Faraday Soc., **9**, 281 (1914).

[43] Schulze: *Ibid.*, p. 270.

[44] Kuessner: Zeit. Elektrochemie, **16**, 754 (1910)
Marino: Gazz. chim. ital., **35** II, 193 (1905).

[45] Marino: Zeit. anorg. Chem., **39**, 152 (1904).

[46] Müller, W. J.: Zeit. Elektrochemie, **10**, 929 (1904).

[47] Ruer: *Ibid.*, **11**, 671 (1905); **14**, 309, 633 (1908).
Zeit. phys. Chem., **44**, 81 (1903).

[48] Coehn and Jacobsen: Zeit. anorg. Chem., **55**, 335 (1907).

[49] Poggendorff: Pogg. Ann., **74**, 587 (1849).

[50] Schönn: Zeit. anal. Chem., **10**, 291 (1871).

[51] Some papers on the general subject of passivity are given.
Bernouli: Dissertation, Munich.
Caspari: Zeit. phys. Chem., **30**, 89 (1899).
Michell: Arch. Sci. phys. et nat. (4) **10**, 122 (1900) (on chromium).
Elbs and Nübling: Zeit. Elektrochemie, **9**, 776 (1903).
Brauer: Zeit. phys. Chem., **38**, 441 (1901) (on chromium).
Nernst and Lessing: Chem. Zentr. (5) **6** II, 241 (1902).
Burgess: Trans. Am. Electrochem. Soc., **4**, 31 (1903).
Foerster and Piguet: Zeit. Elektrochemie, **10**, 714 (1904).
Muthmann: *Ibid.*, **10**, 521 (1904).

Summing up now, we find that passivity of metals is developed through or by oxidation processes.

A passive rod of iron may passivate another piece by immersing a sufficiently small surface of the active rod in a solution with the passive rod which is in electrical contact. If the surface of the active rod is too large the whole will be active instead of passive. So far as the facts are at hand, it seems that most passive metals really dissolve slowly, while chromium becomes passive and dissolves less rapidly, namely, with a higher valence. Increase in temperature tends to prevent or destroy passivity. The passive state is destroyed by making the metal cathode or by treating with reducing agents.[52] This process is preceded by a period of induction. Passive iron is made active by scratching or touching with a less noble metal (arranging conditions so that the iron may be cathode with sufficient current). There are degrees of activity or passivity, and the transition from one to the other is a gradual one. Passive iron (and presumably passive metal) shows photo-electric fatigue, and some passive metals show electro-static capacities. The appearance of the passive state is exactly as the active state, except in alkaline solutions. A measurable difference in the reflecting power is not found in two pieces of iron polarized cathodically and anodically respectively.

Fischer, F.: Zeit. phys. Chem., **48**, 177 (1904).
Hollis: Proc. Camb. Phil. Soc., **12**, 253, 462 (1904).
Holtz: Physik. Zeit., **6**, 480 (1905).
Winkelmann: Drude's Ann., **17**, 589 (1905).
Sakur: Zeit. Elektrochemie, **12**, 637 (1906).
Zeit. phys. Chem., **54**, 641 (1906).
Lorenz and Hauser: Zeit. anorg. Chem., **51**, 81 (1906).
Jour. Iron and Steel Inst., **4**, 922 (1906).
Gordon and Clark: Chem. Ztg., **30**, 911 (1906).
Lewis: Jour. Am. Chem. Soc., **28**, 158 (1906).
Luther: Zeit. Elektrochemie, **12**, 596 (1906).
Zirnité: Chem. Zeit., **12**, 355.
Haber and Maitland: Zeit. Elektrochemie, **13**, 309 (1907).
Schoch: Trans. Am. Electrochem. Soc., **14**, 99 (1908).
Kreusler: Chem. Ztg., **32**, 476 (1908).
Krassa: Zeit. Elektrochemie, **15**, 490 (1909).
Dunstan and Hill: Jour. Chem. Soc., **99**, 1835 (1911).
Kistiakowsky: Zeit. Elektrochemie, **16**, 881 (1910).
Int. Cong. for Gen. Chem. (London), 1910.
Byers and Voris: Jour. Am. Chem. Soc., **34**, 1368 (1912).
Friend: Jour. Chem. Soc., **101**, 50 (1912).
Armstrong and Colgate: Jour. Soc. Chem. Ind., **32**, 394 (1913).
Byers and Langdon: Jour. Am. Chem. Soc., **36**, 2004 (1914).
Rathert: Zeit. phys. Chem., **86**, 567 (1914).
Flade: *Ibid.*, **76**, 513 (1911); **88**, 569 (1914).
Met. Chem. Eng., **11**, 12, 679 (1913).
Young and Hogg: Jour. Phys. Chem., **19**, 617 (1915).

On rusting of iron and passivity, see
Mugdan: Zeit. Elektrochemie, **9**, 442 (1903).

[52] Flade and Koch: Zeit. phys. Chem., **88**, 307, 569 (1914).

The passivity of metals has called forth probably more experimental work than any other portion of the science of the same importance. Especially noticeable is this, since most of the experimenters agree that a satisfactory explanation has not been reached. Faraday's oxide or oxygen theory was generally accepted until Hittorf showed that chromium became passive, or noble, but still dissolved quantitatively in most solutions as hexavalent ion. The oxide film theory which was developed more fully by subsequent workers postulates that a film of oxide covers the surface of the iron and protects it from the action of the electrolyte. When this oxide is reduced the metal becomes active.[53]

There has been tabulated quite a formidable list of objections to this theory. The following presents the most weighty ones.

In the case of iron and chromium the oxides must be other than the known oxides, and they must be unstable.

The oxides must be good conductors of electricity.[54]

It is claimed that the oxide must be endowed with properties, contrary to what existing phenomena would lead us to expect. For instance, the oxide is reduced by raising the temperature, or placing it in the air.

Le Blanc[55] claims that when metal anodes form insoluble compounds with the anion of the electrolyte they may be made to exhibit the Luckow phenomenon.[56] This consists in adding to the solution a small quantity of a salt, whose anion forms with the metal a soluble salt. Under these conditions the soluble salt is formed and diffuses back and forms the insoluble one by double

[53] A list of papers leaning to this view not given elsewhere follows:
H. von Helmholtz: Messungen und die Fortpflanz, der Reizung in den Nerven, Vol. **2**, p. 764.
Heathcote: Zeit. phys. Chem., **37**, 368 (1901).
Haber and Bruner: Zeit. Elektrochemie, **10**, 698 (1904).
E. Müller and Spitzer: Zeit. anorg Chem., **50**, 321 (1906).
Zeit. Elektrochemie, **11**, 923 (1905).
Haber and Goldschmidt: Zeit. Elektrochemie, **12**, 49 (1906).
Haber: Zeit. anorg. Chem., **51**, 356 (1906).
Haber and Zawidzki: Zeit. phys. Chem., **78**, 228 (1911).
Ruer: Zeit. phys. Chem., **44**, 109 (1903).
Ostwald: See below.
Manchot: Ber., **42**, 3942 (1909).

[54] Ostwald: *Abhand der Math. phys. König. Sächs. Ges. d. wiss.* **25**, No. 4 (1899); **26**, No. 2 (1900).
Zeit. phys. Chem., **35**, 33, 211 (1900).
Zeit. Elektrochemie, **7**, 635 (1901).

[55] Le Blanc and Binschedler: Zeit. Elektrochemie, 8, 255 (1902).

[56] Isenberg: *Ibid.*, **9**, 275 (1903).
Just: *Ibid.*, **9**, 547 (1903).

decomposition in the solution. Thus the insoluble salt sinks away from the anode and does not form a film over it. No such precipitates have been noted in the cases of iron and nickel in acid solutions, or in neutral solutions[57] where without the addition of the second salt, the metal becomes passive.

In the measurement of anodic polarization there is no break in the voltage current curve corresponding to a definite oxide.

It is claimed that an oxide would not give such a noble potential.

And lastly, there can be no oxide present because if it were present it would change the reflecting power of the metal. There is no difference in this property in active and passive iron.

Rather than face such objections only a few of which have been given, the majority of investigators have rejected the oxide theory.

After working with chromium Hittorf suggested that passivity was due to a change in the surface of the metal. He developed no theory, however. Finkelstein[58] developed the so-called "valency theory" which postulates that the metal, with different valences, is present in quantities, depending on the conditions of temperature and other factors. The behavior of a metal anode will depend on the relative concentrations of these modifications. Attempts have been made by W. J. Müller to find evidence for this theory in a consideration of the electron theory of metallic conduction. Hittorf[59] and Byers[60] favor the view that the metal is changed, but do not venture a guess at the character of the change. The futility of such a theory is apparent when we consider that Finkelstein assumes that at the surface of iron are present both ferric and ferrous iron. The ferric iron is noble. Ferrous iron dissolves leaving an excess of ferric and the anode is passive. If, however, the conditions are such that ferric is transformed rapidly into ferrous the anode is active for the surface does not become covered with an excess of ferric ions. Müller considers the passive iron to be hexavalent. The cause of passivity is to be sought within the electrode itself. In other words the character of the solution would not change in any

[57] Le Blanc and Levi: Zeit. Elektrochemie, **11**, 9 (1905).

[58] Finkelstein: Dissertation, Göttingen (1901).
Zeit. phys. Chem., **39**, 91 (1901).
W. J. Müller: *Ibid.*, **48**, 577 (1904).
Zeit. Elektrochemie, **10**, 518 (1904); **11**, 755, 823 (1905).

[59] Hittorf: *l. c.*

[60] Byers: Jour. Am. Chem. Soc., **30**, 1742 (1908).

way the phenomena of passivity. This being just contrary to what is actually found, and in view of the fact that there is no sudden change in voltage showing the appearance or disappearance of one or another modification, the theory has not been supported. It is also open to the rather serious objection that the whole thing is a fiction of the imagination founded on very little fact, and is very poorly developed.

Le Blanc[61] has developed the so-called "reaction velocity" hypothesis which postulates that, the passage of the metal into the ionic state is a reaction accompanied with a chemical change which may or may not be rapid. If slow, the metal is passive, and *vice versa*. The chemical change is either a reaction of the metal with the discharged anion,[62] or, according to Le Blanc, it may be the hydration of the ion, thus:

$$\text{Ion} + \text{water} \leftrightharpoons \text{ion hydrate.}$$

When this reaction is slow, polarization sets in until the potential becomes so high that oxygen may separate. This interesting theory, which in general (reaction velocity) expresses one of the properties of passive metals, is based on an assumption highly improbable, viz.: that the hydration of the ion takes place slowly when the anode of iron is in sulphates and nitrates, but rapidly in chlorides. Furthermore, after one's credulity is thus strained, it must be believed that the reaction of ion hydration must be rapid or slow in the same solution under the same conditions.

This would occur in chromic acid solution. If iron made passive in air be placed in this solution it remains passive; active iron placed therein remains active.[63] Thus under identical conditions (because by definition there is no difference between active and passive iron) a reaction may be rapid or slow, which is absurd. Such a theory based on assumptions *ad hoc* should not be taken seriously.

As for the slow reaction of the "discharged ion" with the metal, causing passivity, such a theory is absurd. If active iron

[61] Le Blanc: Boltzmann Festschrift, 183 (1904).
Zeit. Elektrochemie, **6**, 472 (1900); **11**, 8, 705 (1905).
Abhandlungen der Bunsen Ges., No. 3 (1910).
Text book of Electrochemistry, p. 283 (1911).
Trans. Faraday Soc., **9**, 251 (1914).
Reichenstein: *Ibid.*, **9**, 228 (1914).
Sackur: Zeit. Elektrochemie, **10**, 841 (1904).
Brochet and Petit: *Ibid.*, **10**, 909; Bull. soc. chim. (3), **31**, 742 (1904).

[62] Sackur: Zeit. Elektrochemie, **14**, 607 (1908).

[63] Schmidt: Trans. Faraday Soc., **9**, 263 (1914).

is made anode in sulphuric acid, solution of the iron goes on to some extent; the metal then becomes passive, and the solution of the iron drops to a minimum. Suppose we assume that this minimum represents the solution due to the slow reaction above. The iron dissolved more rapidly at first, and we are at a loss to know why its solubility decreased. It may be seen, therefore, that the above mentioned theory, assuming that anions were discharged, is simply a statement of the proposition, rather than a solution of the problem.

Furthermore, regarding the views of both Le Blanc and Sackur it may be said that iron as anode may be made passive by opening and closing the circuit at current densities where it would continuously dissolve if the current flows uninterruptedly.[64] Heathcote says "it behaves as if one could teach it to become passive." It is absurd to consider that the conditions are changed, by opening and closing the circuit, so that the reaction of the discharged ion (assumed) with the metal, or of the ion hydration, is slowed down. Rather, since diffusion is allowed, the reaction should be increased.

Shortly after the above view of the situation was published, Fredenhagen developed the so-called oxygen charge or oxygen film theory.[65] He polarized an anode and found that the polarization potential rose gradually. There were no sudden breaks in the voltage current curve. He assumed that the polarization was due to the slow reaction of the metal with oxygen and the oxygen builds up forming an oxygen film over the surface of the electrode. The investigator assumes the presence of oxygen at the anode, for when hydrochloric acid or chlorides are added and electrolysis carried on, hypochlorite (sic) is obtained. It is assumed that the discharged chlorine reacts with the oxygen of the film. It is considered that the oxygen or oxide is present as a solid solution in the metal. Thus an increase in temperature would drive out this oxygen and render the iron active. It would explain the negative effect obtained by measuring the reflection of light by the active or passive condition of the iron.

[64] Heathcote: *l. c.*

[65] Fredenhagen: Zeit. phys. Chem., **43**, 1 (1903); **63**, 1 (1908).
Zeit. Elektrochemie, **11**, 762, 857 (1905).
Mugdan: *Ibid.*, **9**, 442 (1903).
Muthmann and Frauenberger: *Sitzungsber. kgl. bayr. Akad.*, **34**, 201 (1904).
Zeit. Elektrochemie, **10**, 929 (1904).
Flade: Zeit. phys. Chem., **76**, 513 (1911).

On the other hand, the really serious objection to this theory is that it postulates a slow reaction between a metal and active oxygen. We know, however, that magnesium is passive and yet it is acted on by atmospheric air. Iron rusts readily, but we are asked to assume that it reacts only slowly with nascent oxygen. One would hardly grant that for the sake of argument.

Tomlinson[66] assumed that the passivity of iron was due to its extreme cleanliness.

Reviving this idea, Foerster[67] assumes that iron is normally passive, and that activity is due to the presence of a catalytic agent. The reasoning according to Grave[68] is not at all convincing. He assumes, however, that hydrogen ion is the catalytic agent. Without going further into an unprofitable theory we may say that Flade and Koch[69] have heated active iron in a vacuum. After heating, the iron was still active, which shows that the hydrogen has nothing essential to do with the phenomenon. This result is just contrary to the experiments of Grave, who found that iron heated in a vacuum at 357° C. for one-half hour became more noble by 0.1712 volt. This forces us to discard the work of Grave, who also found that iron became passive, or more noble by 0.2122 volt, after heating to a white heat in nitrogen. The contradiction mentioned above, together with the fact that in all of Grave's experiments of heating iron, only when hydrogen formed the atmosphere, was the iron active, led us to believe that in the experiments the iron came in contact with the air after heating. Thus pure iron, prepared by heating in nitrogen, on being exposed to air would acquire a film of oxide spontaneously. This would protect it and make it more noble in the tenth normal potassium hydroxide used in measuring the potential. In the case of heating in hydrogen, this gas might have protected the metal from oxidation so that a film of the proper thickness would not form.

In view of the fact, too, that no analyses are given of the nitrogen used by Grave, and in view of the fact that it is one of the most difficult gases to obtain free from oxygen, it seems from

[66] Jour. Chem. Soc., **22**, 141 (1869).

[67] *Foerster: Abhandlungen Bunsen Ges.*, No. 2 (1909).

[68] Grave: Zeit. phys. Chem., **77**, 513 (1911).
Rathert: *Ibid.*, **86**, 567 (1914).
Schmidt and Rathert: Trans. Faraday Soc., **9**, 257 (1914).

[69] Flade and Koch: Zeit. Elektrochemie, **18**, 335 (1912).

the simple procedure used, that oxygen could unquestionably be present. We have found that it is a most difficult problem to keep oxygen out of gaseous nitrogen in carrying out high temperature work. In fact we have probably never been able to keep out traces of this gas. The slightest trace of moisture in the presence of red hot iron will certainly give oxide. We feel therefore that it is impossible to accept the statement that iron would become passive if heated in pure nitrogen, especially in view of the fact that the critical experiment upon which Grave bases his theory, has been shown to be wrong.

Having seen that the theories given above are none of them satisfactory as stated and developed, let us start at the beginning and see what can be accomplished. All processes of developing the passive state of metals are oxidation processes. The phenomenon must, therefore, be due to oxidation. Oxidation may be considered from four standpoints. These will be considered and discussed in turn. We prefer not to consider the "so-called" "reaction velocity" hypothesis other than a statement of the problem.

1. In the first place oxidation from the electrolytic standpoint consists in adding a positive charge to an ion. It might be assumed therefore that the process was one of increasing the valence of the metal at the surface, without effecting chemical combination. This gives us the valence hypothesis in slightly different form. If the valence could be increased, it would be accomplished by adding positive charges to the metal atoms in the solid film. This would mean making ions of them *in situ*. As a matter of fact the passive condition is always preceded by preliminary solution of the metal. When iron is made anode in sodium hydroxide solution, for instance, there is a preliminary solution of the metal. Since the amount of preliminary solution may be anything, depending on the conditions (rapid rotation in concentrated nitric acid)[70] there seems to be no reason for assuming that metal of two valences is present or is formed, one of which dissolves leaving the other.

Furthermore, if it is possible to change the valence of the iron, some condition should allow the total conversion of the iron to the noble valence. No case, however, has ever been noted where

[70] See below.

more than the surface film has been affected. This ingenious hypothesis seems, therefore, to have been founded less on fact than fancy. We may also add that a close study of the solution and deposition of metals leads us to the inevitable conclusion[71] that when a metal is deposited the ion loses its charge or charges. It is then analogous to metal vapor, or in the atomic state. These free atoms then combine to a complex representing the liquid state, and then to one representing the solid, finally crystallizing. Solution would be the reverse process all along. The complex would dissociate to the atom which would assume a positive charge, and thus become an *ion in solution.* According to our view, to explain polarization in copper sulphate-copper electrolysis,[72] for instance, we must assume that copper ionizes first, with the assumption of one positive charge. This condition is unstable, and therefore another charge is added. However, if a high current density be used the anode furnishes largely cuprous ions. This is probably due to the fact that with high current density, the migration of acid ions is not sufficient to make the solution at the anode strongly acid. Thus the cuprous ions are more stable and are therefore formed. When the cuprous salt mixes with the bulk of the electrolyte it decomposes separating cuprous oxide or finely divided copper. We believe, therefore, that a metal atom dissolves, assuming the smallest number of charges whereby it may become an ion. If it is stable in this state, it will remain so until complete solution is effected, or until the conditions are changed so that it may become oxidized. Thus iron dissolves as ferrous ion, the oxidation to ferric taking place only after there is no more metal to dissolve.

We are therefore forced to the conclusion that in the solid metal there can be no distinction between ferrous and ferric iron. All particles are the same and the solution or ionization takes place as ferrous which may or may not be oxidized to ferric, depending on the conditions. The above view of oxidation causing passivity may be dismissed.

2. Oxidation may be considered as removing hydrogen. This cannot cause passivity for Flade and Koch removed the hydrogen from active iron by heating in vacuum, and still found the iron active. This view cannot therefore be considered.

[71] Bennett and Thompson: Trans. Am. Electrochem. Soc., **29**, 269 (1916).
[72] Bennett and Brown: Trans. Am. Electrochem. Soc., **23**, 389 (1913).

3. The next step in the four possibilities is that oxygen might be set free. The process of oxidation might be the generation of an oxygen layer over the surface of the metal. Aside from the fact that we cannot admit that oxygen can be present at the surface of magnesium without entering into combination with it, we find it difficult to see how iron in the air may sometimes acquire the film of gas, to make it passive. This would require that massive metal would condense this gas on its surface. We could see how oxygen could be driven into the metal by the electric current, but we cannot see how, by chemical solution, the gas could accumulate either as a solid solution in the metal which it has not reacted with, nor will react with, or as a film over the metal protecting it. This would require the spontaneous decomposition of the passivifying agent separating oxygen. The presence of oxygen is all that is necessary to induce this decomposition. This view cannot possibly be upheld for we know nitric acid does not decompose in the presence of oxygen, in the dark. It could not therefore form a continuous film of oxygen, covering the surface of an iron rod.

4. This brings us then to the last possibility, namely, that the oxidation is the adding of oxygen to the metal in question, with the formation of a definite oxide which, on the surface of the metal, more or less protects it from action of the solution, since the solution touches the oxide and not the metal itself.

The Faraday hypothesis, however, cannot be accepted for there are too many valid objections to it as it has been developed. Probably the most serious objection to the present "oxide hypothesis" is that the oxide must be stable under certain conditions, and very unstable when the conditions are slightly changed. Let us inquire into the possibility of stabilizing otherwise unstable products, without a change of conditions of temperature, concentration of solution, etc.

We know that if sodium hydroxide be added to a boiling solution of copper sulphate, the black cupric oxide will be obtained. If, however, a small amount of manganese sulphate be present, the black oxide is not obtained but the blue hydrate persists[73] even though the solution be boiled vigorously. The manganese salt is adsorbed by the cupric hydrate and stabilizes it.

[73] Tomassi: Bull. Soc. chim. (2) **37**, 197 (1882); Comptes rendus, **99**, 37 (1884).
Bancroft: Jour. Phys. Chem., **18**, 147 (1914).
Blucher and Farnau: *Ibid.*, **18**, 634 (1914).

Another case strictly analogous to the present problem is the adsorption of this cupric hydrate by wool. Wool boiled in the presence of a copper salt, is dyed green. This is due to the hydrolysis of the copper salt and the adsorption of the cupric hydrate by the wool. The adsorption by the wool stabilizes the cupric hydrate so that it does not decompose and give the black oxide on boiling.[74] By being adsorbed, therefore, we can say that the substance is stable under conditions where it would decompose if alone.

Thus in the case of the oxide which generates the noble potential of passive iron, it is unquestionably unstable as a solid or in solution in water, at ordinary temperatures, for it has not yet been prepared thus. It may be stabilized, however, when in contact with metallic iron. In other words, metallic iron *adsorbs* the oxide, and thus makes it stable.

Adsorption changes with a change in temperature. If adsorption takes place with evolution of heat, it will be decreased by raising the temperature, according to the Theorem of Le Chatelier. A decrease in the adsorption of gases by charcoal[75] is found with rising temperature. In the case of adsorption of dyes by fabric, a number of instances are known where the adsorption passes through a maximum, decreasing beyond this maximum with rising temperature.[76] It is therefore both possible and probable that the adsorption of a higher oxide of iron by iron is decreased with rise in temperature. An increase in the temperature decreases the adsorption of the oxide and that which was stable at the lower temperature becomes unstable and decomposes. The protective oxide would be destroyed, and the metal made active. Besides the decrease in adsorption tending to render the oxide less stable at higher temperatures there is a direct temperature effect on the oxide itself. Several higher oxides of the metals have been prepared at low temperatures. These when brought up to room temperature spontaneously decompose. Thus would the higher oxide of iron tend to decompose with rise of temperature.

It has been urged against the oxide hypothesis that there was no break in the voltage-current curve, showing the appearance

[74] Bancroft: *l. c.*
[75] Freundlich: Kapillarchemie, *l. c.*
[76] Bancroft: Jour. Phys. Chem., **19**, 148 (1915).

or disappearance of the higher oxide. We cannot see why the adsorbed oxide should give the voltage of massive oxide unless the surface is completely covered. In other words, when passivity is complete the full voltage is reached. It is analogous to the behavior of a platinum cathode in silver nitrate, for instance, with voltage lower than the decomposition voltage. We obtain back electromotive force measurements of values intermediate between platinum and silver. Thus we obtain values intermediate between iron and the higher oxide, as iron becomes active or passive.

Let us consider this also from the standpoint of the well-known adsorption isotherm, which with changing concentration is a smooth curve, rather than one with definite breaks in it when definite compounds are formed. The reverse of this adsorption isotherm may be considered as the solubility curve of the adsorbed substance. Since the solubility varies gradually all along, the voltage generated by the adsorbed oxides would vary continuously. Consequently, there would be no definite breaks in the voltage current curve.

It has also been urged that an oxide of iron would not give the potential of passive iron. In view of the fact that we know lead dioxide and manganese dioxide are good electrical conductors[77] and give potentials higher than that of passive iron, there is no reason why a higher oxide of iron than those known at the present time should not give such potentials. In fact, we could not explain a low potential if given by reasoning from analogy. The instability of the oxide, with a strong depolarizing power in itself requires the generation of a high negative potential.

Now let us state the new theory more fully. Before becoming passive, iron dissolves in such passivifying agents as nitric acid, and sulphuric acid when the current is used. In fact in all such cases passivity is preceded by a preliminary solution of the iron.[78] This gradually decreases and finally drops to a minimum value, when the iron becomes passive. This preliminary solution of the iron indicates that the phenomenon of passivity is not occasioned by an oxidation of the solid iron surface to the higher oxide directly or *in situ*. If such were the case the passivifying action

[77] Haber and Goldschmidt: Zeit. Elektrochemie, **12**, 62 (1906) have shown that Fe_3O_{11} conducts the current, as a conductor of the first class.

[78] Heathcote: *l. c.*

of nitric acid would decrease as the iron nitrate concentration increased, occasioned by the preliminary solution of the iron. This would follow, for ferric nitrate solution (which is obtained) is not as strong an oxidizing agent as 1.40 nitric acid, for instance. This would mean that 1.40 nitric acid is too strong an oxidizing agent or that iron ion catalyzed the formation of the higher oxide, neither of which are tenable, since active iron does not not become passive in chromic acid solution, althought once made passive it remains passive therein. Furthermore, if the tendency is to oxidize to the higher oxide *in situ,* a rapid removal of the ferric nitrate would tend to increase the speed of the oxidation and would tend to aid in passivifying the piece. As a matter of fact rotation of the piece is known to decrease the passivifying action. We have also found that if a piece of iron wire is fastened in a chuck so as to be "off center," and rapidly rotated, 1.40 nitric acid does not make it passive, but the iron continues to dissolve rapidly.

Since, therefore, the film cannot be formed, *in situ,* it must be formed from the solution side. The oxidizing agent must oxidize the iron up to the higher valence, and the metallic surface adsorbs the higher oxide. The iron probably ionizes as ferrous, is immediately oxidized to ferric, and some ions are taken up higher to form the higher oxide. This is then adsorbed by the iron. The rapid stirring, therefore, removes the ferric ions before they can be further oxidized, and therefore the iron remains active.

It may be asked, at this point, why the iron is oxidized to the higher oxide at all when metallic iron is present to dissolve. It might be claimed that the potential would never rise high enough to accomplish the oxidation. As the speed is increased, the voltage at which the process is carried out is likewise increased. Furthermore as the concentration of iron ions in the solution increases it requires more work to force more into the solution. The concentration of iron ions is probably very high over the surface film of the anode under conditions for the development of the passive state. Under these current conditions, the iron ions sent into the solution are probably more than equivalent to the sulphate ions brought up to the anode in the case of the development of passivity as anode in sulphuric acid. The hydroxyl, or oxygen, ions will probably carry a part of the current. This

means that at these rather high current densities there will be a partial formation of oxide or hydroxide of iron, which as a film, would further tend to hinder solution of the anode. Three factors, namely, the increase in the speed of the process, the building up of the products of the reaction, and the development of a basic condition with a film of a normal oxide or hydroxide of iron, tend to raise the voltage of the anode process and therefore tend to develop conditions for the formation of a higher oxide which may protect and make the metal more noble. By rapidly stirring, these conditions are overcome. Moreover, when the process of solution as anode is slow, the conditions above are not developed. When the current density is low iron may dissolve and diffuse away, the potential never becoming high enough to form the higher oxide.

According to this view, the Luckow phenomenon, referred to above, could not be expected to take place. When the iron ions which have been oxidized to the higher valence are removed from the surface of the iron they are unstable and break down. Suppose we consider a strong solution of nitric and hydrochloric acid, with an iron anode. Suppose also that there was formed ferric chloride which diffuses back, and let us assume, for the sake of argument, that the nitric acid oxidized the ferric iron to the higher oxide. In the absence of hydrochloric acid it could not exist in measurable quantities at ordinary temperatures unless in the presence of iron (metal). Another cause of its decomposition would also be found in the hydrochloric acid present. Just as hydrochloric acid decomposes lead and manganese dioxides, so would it decompose the higher oxide of iron. No passivity can be obtained when this acid is present.

Iron which has been made passive and is noble may become less so by standing in air or by being placed in a vacuum. This follows from the theory above. The higher oxide gradually dissolves in the liquid film, and decomposes. When the piece becomes dry it is stable and can be kept so practically indefinitely. The instability wet is therefore due to solubility of the oxide. Thus the metal is said to dissolve slowly in the reagent which develops and maintains passivity. In potassium nitrate solution the life of the adsorbed layer is very short. Here as well as in air and vacuum, the passive state is not being maintained by the

formation of more of the higher oxide as in the case of strong nitric acid. The phenomenon is therefore dynamic as has been said above. In the case of some solutions where the passive iron becomes rapidly active, it may not be due entirely to a solution or decomposition of the oxide. The iron may strongly adsorb one or more of the ions in the solution and thus displace the adsorbed oxide. We know of many cases of such displacement in adsorption. When arsenic sulphide[79] is coagulated with barium chloride and the precipitate treated with calcium nitrate, no barium is left in the precipitate, it being quantitatively replaced or displaced by calcium.

Thus the adsorption of the higher oxide may be decreased until the potential is changed to positive and the iron becomes active. Passive iron does not have its oxide film reduced by air, but it merely decomposes, liberating oxygen, just as many substances liberate oxygen by being oxidized to higher oxides which decompose,[80] the substances going back to the original oxide.

The fact that iron as anode may be passive, but when the current is broken it becomes active, is in accord with the theory. As long as oxide is being formed and adsorbed the iron is passive. When the forming of oxide ceases the reverse reaction of solution and decomposition predominates and the iron becomes active. In the same way if this reaction is slow only a small amount of oxide must be formed to counteract it, and therefore after passivity has been accomplished at the anode, a very small current serves to maintain this state.

The reason iron is not passivated by chromic acid chemically, but is as anode in this acid, and furthermore, when passive will remain so in the acid, is found in the fact that as iron dissolves in chromic acid hydrogen is set free *at the surface of the iron.* This lowers the oxidizing potential so that the higher oxide is not formed. When, however, the hydrogen is liberated at the cathode rather than at the surface of the iron, the anode becomes passive. The chromic acid is sufficient oxidizing agent to maintain passivity of the iron and, if hydrogen is kept away, it possibly would passivify active iron.

[79] Linder and Picton: Chem. Soc. Jour., **67**, 66 (1895).
See also Freundlich: Kapillarchemie, on organic acids displacing each other.

[80] Unpublished work.
Zeit. anorg. Chem., **50**, 322 (1906).
See also Foerster and Müller: Zeit. Elektrochemie, **13**, 133 (1907).

The objection raised by Königsberger and Müller that attempts to show the presence of an oxide film by the difference in the reflecting power of the anode and cathode of iron is not valid on any ground. In the first place adsorption by solids may take place without markedly changing the appearance of the surface. In the second place there are instances of the presence of oxides where optical means do not distinguish them. Lastly, however, the most serious objection to the work of the above experimenters is that they compared the anode with the cathode as to reflecting power of light. We now know that the liberation of hydrogen[81] at the surface of a cathode results in roughening and darkening the surface so that less light is reflected. Especially would this be true with iron where the adsorption of hydrogen is high. In driving this hydrogen into the metal, the surface must be disturbed. These measurements were therefore made on pieces of metal whose surfaces were unquestionably the same; one, however, was made *matte* by use as cathode, the other as anode.

Now as to the various ways in which activity may be re-established, there is very little that need be said. When passive iron is placed in water or other solutions which tend to induce activity, it is only necessary to remember that the cause which produced passivity has been removed and therefore if the adsorbed oxide decomposes at all, activity must result. Adsorbed substances can be washed out by certain liquids, depending on the substance adsorbed. This may be by straight partition or by replacement. At any rate the concentration of the adsorbed substance would always be zero in the solution, for as soon as it is washed out it would decompose. Thus the iron would be exposed, or become active. Any reducing agent would actually reduce the oxide. Thus reducing agents tend to destroy passivity.[82]

In the same way making the piece cathode would reduce the oxide and render the metal active. Touching with a base metal like copper, zinc or tin, makes the passive metal cathode, reduces the oxide, and renders the metal active. Scratching exposes a certain amount of the metal surface. This gives a local cell in which the iron in the scratch acts as anode while the oxide acts as cathode. Either the scratch is of such a nature that the cur-

[81] Newbery: Chem. Soc. Jour., **105**, 2426 (1914).
[82] Flade and Koch: Zeit. phys. Chem., **88**, 307 (1914).

rent density is low (at the iron bared by scratching) so the iron dissolves as anode, not becoming passive again or, during the operation of scratching, sufficient reduction has occurred at the cathode (the part of the piece not scratched) so that the whole thing becomes active. Both the reduction during the process of scratching, and the fact that the critical current density is not reached on the anode area, probably play a part in the activation by scratching.

The former is indicated by the fact that when a passive dry rod is scratched, and then dipped in acid, it becomes active only on the part scratched. There is certainly no reduction during scratching. This experiment is not absolutely conclusive, however, for we are dealing with a dry film, and therefore the conditions are not the same as with the wet film. In the case of the wet film, the whole piece does become active, and there is probably reduction during scratching, for every condition for a local cell is fulfilled. Iron is continually exposed, and therefore must act as anode, the oxide film being cathode.

After the disturbance due to scratching has ceased the iron will probably continue to function as anode. When a scratch is made the acid which finds its way to the iron must be made dilute by the solution of the iron in it. This tends to decrease its oxidizing power. Furthermore the scratch is probably narrow and the cross section of the acid film is small. Thus the electrical resistance in the circuit of the local cell would be high and therefore the current would be low. Thus a low anode current density in the local cell.

Iron — Nitric Acid — Higher oxide — Iron,

should develop activity.

An experiment was tried to show that cutting the current density down below the critical value at a small spot would cause the rod to become active. Accordingly, a rod was made passive about two inches up from the end. About the same distance further up, a filter paper was wrapped around the rod. By immersing the passive end first the second area was made passive. When the edge of the filter paper was reached the whole became active. This occurred even though the filter paper was wet with 1.20, 1.40 sp. gr. nitric acid, with water or left dry. The cur-

rent density is low due to the resistance of the diaphragm separating the active and passive portions. Iron continues to dissolve and shortly the passive metal is made active. When the area under the paper was covered with an oxide film by heating in the oxidizing flame of the bunsen burner, immersion in dilute (1.20) nitric acid did not cause activity over any part of the rod. When there was no anode of iron, in other words, there was no activity. In scratching passive iron the important effect is the development of a current of low density at the surface of the iron bared, with the adjacent areas acting as cathode, having the oxide layer reduced, while the iron (anode) continues to dissolve.

The pulsation effect is easily explained on the basis of this theory. It is due to local inequalities. One spot acts as anode, the remainder of the piece as cathode. Some time is required for the oxygen to oxidize the iron to the higher oxide and have it adsorbed by the iron. There would be less time lag at the cathode where hydrogen is depolarized by the oxide. This lag in time at the anode would cause the cathode reaction to go further than it would if no such lag occurred. When the anode finally becomes noble, the cathode is less noble and the current changes, and so on, giving rise to pulsations. It would probably be impossible to passivify two pieces of metal connected together without an interchange of passivity and activity, with a consequent flow of current back and forth. This is due to local difference in the metal, namely differences in the physical state of the pieces of metal.

Nichols and Franklin[83] claim that in the magnetic field iron becomes active. Byers[84] has shown that in the magnetic field a higher anodic current density is required to develop passivity than when the field is not operative. Both investigators are probably right. Nichols and Franklin used iron filings, and we have shown that if filings are made passive and placed between the poles of an electro-magnet, and the current turned on, the filings become active. This is due to one piece scratching another, caused during orientation of the particles of iron when mag-

[83] Nichols and Franklin: *l. c.*

[84] Byers and Darrin : Jour. Am. Chem. Soc., **32**, 750 (1910).
Byers and Morgan: *Ibid.*, **33**, 1757 (1911).
Byers and Langdon: *Ibid.*, **35**, 759 (1913).

netized. When a solid piece of iron is passivated in 1.40 nitric acid, and placed in the field, it does not become active. There is probably a tendency to activify, however, which is measured by the increase of anode current density required to make the iron passive when under the influence of the magnetic field. This can be accounted for by the effect of the field upon the metal itself. The field must pulsate, causing a pulsating effect in the particles at the surface of the metal. This would disturb the adsorbed film and therefore tend to expose the metal. The field also effects a considerable stirring of the solution. This decreases the tendency to passivify, and Byers concludes that this latter effect is sufficient to explain the difference.

According to the view of passivity taken, it becomes easy to explain certain facts which have been known for a long time. In the experiment of Herschel, for instance, where an iron rod was divided into two parts by a band of wax around the rod at the center, after inducing passivity on both ends of the rod, activity was restored on one end only when that was touched with copper, the whole being in air; when both ends were in acid and one end touched, the whole becomes active. When the rod is touched with the base metal in air, it becomes cathode, the base metal anode, the film of acid being the electrolyte. Since, however, the acid does not wet the wax, thereby forming no film over it, the cathode area extends over one end only. Consequently only one end, namely, the end touched, becomes active. When, however, the rod is immersed in the acid the electrolyte is continuous and both ends of the rod may now act as cathode. Consequently both ends become active under these conditions.

When a piece of passive iron, held in air with a film of acid over its surface, is touched with a base metal or scratched it becomes active, the activity spreading gradually so that it can be followed by the eye. This slow development of the active state is due to the fact that the electrical resistance of the film of acid is high. It seems therefore that an area is made active by an adjacent portion acting as anode, and so on until the whole is active. In other words, the quantity of current flowing from the end touched to the opposite end of a piece during the operation is negligible, due to the high resistance of the acid film.

When, however, the piece is immersed in acid and touched,

there is no such gradual spread of activity as noted above, but the whole becomes active practically at once. Here the acid (electrolyte of the local couple) is a good conductor, offering practically no resistance to the passage of the current. The current is therefore more uniformly distributed and the spread of activity is more rapid. In some cases it can hardly be followed by the eye.

Schönbein's experiments are also explained simply. Using the source of current at his disposal, he could obtain passivity anodically under the conditions of concentration of acid, etc., only when he closed the circuit by lowering the iron rod into the acid. When it was closed otherwise the current density was not so high as when the rod was lowered into the acid. It is very probable, therefore, that the critical current density was reached in one case and not in the other. By lowering, the rod became passive progressively. This is made possible since a very small current serves to maintain the passive state, once it has been developed.

It was also noted that if the passive iron was touched with the cathode of platinum, for instance, it became active. This is just reversed from the behavior when no current flows. It is due to the fact that the hydrogen separated at the cathode, which is touching the passive iron, reduces the oxide and the piece becomes active. In other words, the action is the same as iron in chromic acid. It remains active so long as hydrogen is liberated at the surface of the metal. When it is removed to the cathode away from the iron, the latter becomes passive.

In "transmitting" passivity to other rods in electrical contact, and dipped in the same acid, or in passivifying more of a rod by immersing the passive end first in acid, Schönbein noticed that the whole arrangement was passive or active, depending on the relative areas of the surfaces of the passive and active iron. Here it must be remembered that there is a definite quantity of the oxide formed, depending on the conditions. This can depolarize a certain quantity of hydrogen, and leave enough to protect the iron from vigorous action of the acid. When too much of the oxide film is used up, the whole will become active. This is accomplished by the use of too much anode surface. In other words, before the large anode can be made passive, the

oxide on the cathode portion is used up, and the whole is active. When the anode area is less, it is evident, the whole will become passive. We have found that if a rod is made passive in 1.40 nitric acid, an active surface considerably greater than the passive area can be rendered passive by dipping carefully in 1.20 acid. When the active surface becomes too great the whole becomes active.

It has been noted by Heathcote that if passive iron is touched with a base metal the pulsation of activity is down and back and not up and back to the point touched. This is simple; when a rod is held vertically in air with an acid film over it, this film is thickest at the lower part of the rod because gravity tends to pull it down. There is, therefore, less resistance to the flow of current down than up and consequently more current will flow down, and the activity will begin at a point contiguous to and just beneath the zinc. Thus this portion also acts as anode and the activity spreads down rather than up because the upper part acts more like a dry rod. The range of passivity would then spread back to the zinc and the operation be repeated.

When the passive rod is disturbed under the surface of the acid, the tendency for pulsation would also be down and back, for any ferric nitrate formed will run down the rod, since the density of the solution is greater. The depolarization, or oxidation power of the solution below will be less than that above the point disturbed, and therefore the same current would induce activity sooner below than above the point touched. The resistance of the electrolyte is not a factor here. It has also been noted that the potential of passive iron is numerically lower in an acid solution containing ferric nitrate than in the acid without the iron salt.

Heathcote has also noted that iron can be made passive in sulphuric acid at current densities below the critical value, if the circuit is opened and closed, intermittently. This is probably due to the fact that while the current is flowing, and iron ionizing from the surface the adsorption of the higher oxide is disturbed. This may be occasioned by the direct change of surface by solution of the iron, or probably by a change in the rate of removal of the oxide formed in solution. When the rate of solution of iron is cut down, the rate of removal of the anode product by the

flow of the more concentrated solution down the anode surface is decreased. Thus more time is given to adsorb the oxide. By opening the circuit and decreasing the disturbance at the surface such oxide as has been formed may be adsorbed. Thus partial passivity has been induced, where no such effect would have been obtained if the surface disturbances had been maintained. By repeating the operation added increments of the adsorbed oxide are obtained, until finally passivity is induced.

Fredenhagen has noted that a passive iron anode yields a substance when chlorides are added, which evolves oxygen. He concluded that it is hypochlorite and is occasioned by the interaction of the *oxygen film* at the iron anode, with the discharged chlorine. Such an assumption is not needed, since we know that hydrochloric acid (which would be formed at the anode) decomposes higher oxides (PbO_2 and MnO_2 for instance) and that chlorine (which might be set free at the anode) evolves oxygen from higher oxides (H_2O_2 for instance). The latter is probably a direct replacement just as zinc replaces copper ion from sulphate solution. This is now under investigation.

Having decided that the facts of passivity can best be explained by the assumption of an adsorbed film of a higher oxide of iron than is now known, it only remains to show what the oxide is.

It is noted[85] that as anode in dilute alkali, iron gives a bluish green solution, at boiling temperatures, before passivity sets in. When the anode is passive, it is coated with a black deposit of velvety appearance.

Müller and Spitzer[86] have shown that from an alkaline iron tartrate solution a reddish brown deposit may be obtained at the anode, which gives very nearly the potential of passive iron. They say that sufficient quantities could not be obtained for analysis. In other words in small concentrations this oxide becomes stable in alkaline solutions even though iron is not present. It is probably adsorbed by the brown oxide which makes up the mass of the deposit.

Armstrong and Colgate[87] have shown that when iron is dipped in a sulphuric acid solution containing hydrogen dioxide it is covered with a black deposit. When removed, washed with water

[85] Krassa: Zeit. Elektrochemie, **15**, 490 (1909).
[86] Müller and Spitzer: Zeit. anorg. Chem., **50**, 353 (1906).
[87] Armstrong and Colgate: Jour. Soc. Chem. Ind., **32**, 394 (1913).

and then dipped in hydrogen dioxide alone, the deposit is changed to red or to ordinary rust. They have also noted that an iron anode in sulphuric acid is black previous to passivity. It clears up and becomes passive. It is probable therefore that larger quantities of the higher oxide are formed than are used in inducing passivity, or that are adsorbed.

The composition of this oxide under conditions where iron is passive will probably have to be determined indirectly. As a starting point, however, it seemed best to select a solution where we know the iron is in a higher state of oxidation than ferric, and see if suspending a piece of iron in this solution would not cause it to adsorb the oxide and be passive. Accordingly, potassium ferrate was prepared by grinding intimately 3 parts of potassium nitrate with 2 parts by weight of powdered iron. This was then heated to a red heat when an energetic reaction went on evolving quantities of fumes. The mass was cooled and digested with cold water. A dark amethystine solution resulted when the reaction occurred in the proper manner. A few times, due to imperfect grinding and mixing of the original materials, a green solution, probably ferrite, was obtained.

An iron rod was dipped in the amethyst-colored solution and allowed to remain for a short time. It was then carefully removed and dipped in distilled water, and finally tested for passivity by dipping in 1.20 nitric acid according to Heathcote. The rod did not dissolve, and was therefore passive. Thus the oxide cannot be higher than FeO_3, because this oxide develops the passive state when the metal is placed therein.

It only remains now to mention one or two facts concerning chromium especially. Chromium, we have seen, dissolves as anode when passive, as hexavalent ion, thus differing from iron. When active it dissolves as bivalent ion. The active condition is unquestionably the untrammeled solution of the anode, the atom assuming two positive charges. The oxidation to a higher form, when passive, shows that there is some interference under these conditions. The potential is higher, due most likely, as in the case of iron, to an oxide film, since the same objections apply to the several theories in the case of chromium as with iron.

Here also it seemed best to induce passivity as was done in the case of iron with potassium ferrate. Chromic acid and sodium

chromate were taken. In both solutions chromium, which dissolved readily in hydrochloric acid, became passive after about five minutes' immersion and then washing with water. It did not dissolve in the concentrated hydrochloric acid for several minutes. In this case, therefore, the oxide cannot be higher than CrO_3, for this oxide induces the passive state. Since this oxide is soluble it is probable that the metal forms with the chromate radical chromium chromate,[88] which forms the film, the composition of the oxide being CrO_2. Since iron replaces hydrogen from chromic acid, chromium certainly would. The product CrO_2 would therefore be formed immediately which when adsorbed would make the metal passive. Now when this is anodically polarized, CrO_3 is formed by oxidation, and being soluble, is dissolved. Thus chromium when passive dissolves as hexavalent ion. In the case of iron the higher oxide is not readily soluble, and therefore the solution of the iron is not quantitative according to Faraday's law.

At this point attention should be called to the analogy of chromium to lead. Lead unquestionably becomes passive due to the protecting film of lead dioxide. In this case, however, it is stable and every one admits its existence and protection as a film over the lead. However, when the temperature is low and the concentration of sulphuric acid high[89] the lead dissolves as tetravalent ion.

We have noted that chromium dissolves in hydriodic acid. As in the case of iron in chromic acid, hydrogen is separated at the surface of the metal. This cuts down oxidation so that oxide films cannot be formed.

When, however, the hydrogen is separated at the cathode, the chromium being anode, the latter becomes passive, probably being covered with CrO_2 due to depolarization of what oxygen was present. The iodine is liberated at a low potential, so that the oxidation tendency is low at the anode. In this way the film is not oxidized to CrO_3 and therefore does not dissolve. The chromium, therefore, becomes indifferent, like iron, when made anode in potassium iodide. Hittorf's so-called *"experimentum crucis"* is not therefore in any degree such. The conditions are the same

[88] See Storer and Elliott: Jour. prakt. Chem., **90**, 288 (1863). Carveth and Curry: Jour. Phys. Chem., **9**, 375 (1905).

[89] Elbs and Fischer: *l. c.*

with the exception that hydrogen is present in one case and not in the other, as has been shown above. This is more than sufficient to explain the different behavior, for we know that nascent hydrogen will reduce the oxides which render these metals passive.

From the above the following may be concluded:

1. The general field of passivity, especially that of iron and chromium, has been reviewed.

2. References to previous work have been appended.

3. The passive state of metals is really a slowly dissolving state.

4. Some metals, chromium, magnesium, and manganese, for instance, dissolve as anode when passive with a higher valance than when active.

5. The different behavior of chromium and iron (representing the two types of action) as anode cannot be explained on theories heretofore put forward.

6. All these theories are objectionable.

7. Oxidizing conditions develop passivity.

8. Reducing conditions develop activity.

9. In alkaline solutions, passivity is many times accompanied by a visible film over the surface of the anode.

10. There are no facts which would support the view that passivity is due to one cause in alkaline, and another cause in acid solutions.

11. In all cases, passivity is due to oxidation.

12. Oxidations in the sense of (1) increasing the valence, (2) removing hydrogen, or (3) of adding oxygen as a film, have been shown to be untenable.

13. The formation of an oxide as the result of oxidation is arrived at by elimination.

14. This oxide forms a film over the metal by being adsorbed by it. This film protects the metal, and gives its properties to the metal surface.

15. This oxide is unstable in most cases, but is stabilized by adsorption by the metal.

16. The oxide in the case of iron is higher than known oxides, but not so with chromium.

17. The nobility of the surface, the gradual change of electromotive force, and the instability at elevated temperatures is satisfactorily explained by this hypothesis.

18. The quantity of oxide required to protect the surface is very small.

19. In the further oxidation of chromium as anode the higher oxide, CrO_3, is formed and chromium dissolves as hexavalent ion, since this oxide is soluble. Iron does not dissolve because any higher oxide which may be formed is not soluble readily. The quantity of iron that dissolves is due to the straight solution and decomposition of the higher oxide. This is not quantitative according to any reasonable valence.

20. The oxide in the case of chromium is not higher than CrO_3, and is probably $CrCrO_4$ or CrO_2.

21. That in the case of iron is not higher than FeO_3, and may possibly be FeO_2, similar to chromium.

22. Passivity of lead has been shown where there was no visible film.

23. The action here is similar to lead where there is a visible film of oxide.

24. Passivity in all cases, therefore, is the coating of the metal, by adsorption, with a film of a higher oxide which, being more noble than the metal, protects it from the action of the solution.

25. We measure the electro-motive force of the oxide instead of the metal.

26. According to this view all the facts of passivity are easily explained.

27. Many conflicting experiments have been explained and thus brought into line with facts.

Ithaca, N. Y.

DISCUSSION.

N. K. CHANEY (*Communicated*): It will add to the clearness of our discussion if we note the exact points of novelty in this paper and wherein the oxide theory as developed here differs from the previous oxide theories which the authors consider unsatisfactory.

In a general way all the oxygen theories, whether assuming the formation of oxide alloys or gas films, may be said to have been foreshadowed in Faraday's own very broad statement that he considered that "the surface of the metal is oxidized or else the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation, meaning by that not an actual oxidation but a relation." Again, "the cause of the phenomena is due to a relation of the superficial particles of the iron to oxygen." Thus Faraday did not limit himself to the restricted conception which the authors designate as the Faraday hypothesis.

The supporters of the general oxidation hypothesis may be divided into two classes: first, those who consider that a superficial protective film of oxide or of oxygen gas is formed, and second, those who consider that the protection results from raising the potential of the electrode either by a solid solution of some definite oxide in the metal or by an indefinite oxygen alloy. The first is a static, the second a dynamic conception of the protective action. This second position, which is measurably within the intent of Faraday's definition, forms the essential basis of Bennett and Burnham's contribution. They have substituted for the rather general notion of a solid solution of metal oxide or oxygen in metal, a concrete and detailed picture of the steps which result in a similar final condition. That is, they state that an unknown higher oxide of iron is formed from the iron, in the solution near the electrode, and that this unstable higher oxide is then adsorbed by the metal, stabilized by this adsorption, and so in turn protects the metal.

If the foregoing analysis of the situation is correct, it is evident that the authors have not overthrown but rather amplified and particularized the oldest of the passivity theories, and that if in

general the older conception is unsound, their special superstructure has a most precarious foundation.

We may now consider the details of this special mechanism by which passivity is to be secured. It seems to the writer that the vital and illuminating feature of this present paper is the emphasis laid upon the peculiar property of adsorption in stabilizing certain unstable bodies. It is the restatement in modern terms of Faraday's expressed belief that both oxygen and acids might exist in intimate relation with iron, steel, and platinum without undergoing combination, *i. e.,* the stabilizing of an essentially unstable condition. Granted, however, this stabilizing property, other possibilities in the way of stabilized protective compounds are not absolutely eliminated. In fact, by direct analogy with the stabilizing of monatomic hydrogen on metal electrodes to account for overvoltage, would come the suggestion that possibly passivity was due to the adsorption and stabilizing of monatomic oxygen. This would, of course, be merely a modified oxygen-alloy theory.

The authors objected to the oxygen-film theory, on the ground that nitric acid could not decompose under certain conditions in such a way as to give up free oxygen. But many electrochemists will accept without hesitation the notion that a low concentration of oxygen ions may exist in solution. The discharge and adsorption of such ions would supply the necessary oxygen atoms.

Where a clear proof of a definite oxide as the cause of passivity exists, it is unnecessary to go further, but it is not clear that the authors have proved that their higher oxide can be formed under the circumstances in which passivity usually occurs. It is also apparent that the various degrees of nobility or potential of the metal surface could be accounted for equally well by assuming various concentrations of monatomic oxygen, and such an explanation could have more universal applicability. Any complete theory of passivity must ultimately include the permanently passive or noble metals, such as platinum and gold. The assumption of a variation in the capacity of different metals for selectively adsorbing and stabilizing oxygen ions, or monatomic oxygen, forms a possible basis of a more universal theory, and frees us from the necessity of postulating the existence of so many differment specific and unrelated oxides performing a common function.

The authors have scarcely done justice to the thoughtfully reasoned oxygen-alloy theories, such as those of Reichinstein, and this was hardly possible in view of the immense ground covered in the paper. But in any final accounting Reichinstein's arguments must be more adequately answered, if the authors wish an undisputed field.

C. W. Bennett: We believe, having made iron passive by dipping it in sodium ferrate, and having made chromium passive by dipping in sodium chromate and chromic acid, that the oxides formed are FeO_2 and CrO_2. This is in line with the passivity of other metals, such as manganese and lead, whose higher oxides are MnO_2 and PbO_2, the only difference being that in the case of manganese and lead the oxides are stable and we obtain them in quantity, while we do not in the other case.

We intend to present later a paper on higher oxides, concerning the distinction between higher oxides which give hydrogen peroxide when treated with acid, and those which give salts of a higher valence when thus treated. This difference is one of stability only. There is no essential theoretical difference between PbO_2 and FeO_2.

W. R. Mott: I have here in my hand a typical example of a metal in a passive state produced by the formation of an oxide film. (This formed aluminum anode was prepared by me in 1903, using a sodium acid phosphate solution.) The film increases in thickness with increase in voltage of formation, as is shown by the proportional increase in weight of plate, by the coulombs of electricity required to form the film, by interference color phenomena (see C. I. Zimmerman, Trans. Am. Electrochemical Society, **5**, 147; **7**, 309), a decrease in capacity and many other tests. This then is a *bona fide* solid film. Calculations of the thickness of film that would be obtained with aluminum under its own single potential without additional external voltage indicates a thickness of about one-millionth of a centimeter, which is fairly small for manipulation and tests.

Again the passive state of aluminum can be shown by changing single potential. I have obtained with an untreated aluminum electrode, in a sodium acid phosphate solution, a single potential, after some hundreds of hours, as low as the usual value of copper

against copper sulphate. I ascribe these varying potentials to the dissolved air (oxygen being the active component). Consistent with the approach of aluminum toward the potential of the noble metals, is also its limited rate of reaction with copper sulphate solution unless the latter contains chloride. Mercuric chloride is a powerful means of making passive aluminum active.

Therefore, using aluminum as anode in suitable electrolytes, it forms a very hard film of a complex structure, as shown by the fact that a portion of the film is insoluble even in normal sodium hydroxide. The film has a porous structure. This was pointed out first, I believe, by C. F. Burgess and C. Hambuechen (Trans. Am. Electrochem. Society (1902) **1**, 147). Electrical endosmose causes flow of electrolyte in a porous medium to be from anode to cathode in this case. For this reason, as an anode the film has the conducting solution drawn out of it by electrical endosmose and the broken pores tend to be repaired and the film becomes highly insulating. But as a cathode the porous film again fills with electrolyte and becomes conducting, as was shown by the researches of Ingalls. The gas theory of insulation, to be of any particular value, should apply to both hydrogen and oxygen. Therefore, in the case of aluminum the formation of a higher oxide than Al_2O_3 is not admissible as a working hypothesis of passivity.

Turning from the typical case of aluminum, it is of interest to observe that for iron and chromium the experimental data obtained by polarization of reflected light are probably defective because the active specimen could have had an oxide film of a porous nature and the closing of the pores would give rise to passive state without much change in the optical properties of the total film. Micheli obtained a material difference in the optical properties of active and passive iron, but not in the case of chromium, which, considering its source, no doubt had quite an oxide film to start with. (Micheli, Archives des Sciences (1900), **10**, 122.)

It seems unnecessary to confine the idea of a passive film to oxides only. It is true that generally the oxide film is the reason for the inertness, but why should not an insoluble fluoride, bromide, cyanide, etc., also produce similar effects?

Dr. H. E. Patten (Trans. Am. Electrochemical Soc. (1904)

6, 9) observed insulation on an aluminum anode with a solution of aluminum bromide in ethyl bromide under conditions where no oxygen was present. Again, if metallic sodium is dipped quickly in concentrated sulphuric acid (Baker's experiment), there is a flash of light and the metal is soon coated with an insoluble film, making the sodium passive for that solution.

In conclusion, then, more research work needs to be done on these very thin films. The metal, as a coarse powder, could be examined as to electrical conductivity in the active and passive states. When Woehler first prepared aluminum as a powder he reported it as insulating, undoubtedly because of the effect of the oxide films. The conductivity of active and passive plates in mercury would give, by contact resistance, information bearing on the nature of the film formed by the action of alternating current. This is a means of separating the film for analysis, with formed aluminum anode plates. The surface tension of various materials, such as mercury, oil, etc., against active and passive metal should be of interest. The degree of adhesion of deposited metal is another line of attack. The investigation by optical methods, color interference, and polarization of light by reflection, can be much extended. There are also methods of determining the number of coulombs required to form the film, and to weigh it on very thin metal sheets.

Finally, I would define passivity as inactivity (chemical and electrochemical) due to an insoluble and impervious film coating the metal.

C. McC. Gordon (*Communicated*): To my mind, the arguments against this old Faraday film theory of passivity have never appeared at all convincing. The authors are to be congratulated for pointing out that the objections to other proposed explanations are even more formidable than those against the film theory. No other theory explains the facts so simply and reasonably as the film theory. Most of the objections to the old film theory hold well against the theory of the authors. The differences between criteria of the old film theory and the theory of the authors are so few that many more crucial experiments than those cited by the authors must be made before the new theory will be accepted in place of the old.

The two strongest arguments presented for the film not being firm *on* the surface of the electrode, are (1) that "passivity is preceded by solution of the iron" and (2) that a rapidly rotated iron rod does not become passive in 1.40 nitric acid.

To the first of these objections it can be replied that it is well known that the iron surface does not become passive at all points at once. Surface irregularities are such that it is difficult to make the last few active points passive. While part of the surface may become passive at once, iron may be dissolving from other points on surface.

The second experiment mentioned, namely, that an iron rod rotated off center does not become passive may also be explained in terms of the *in situ* theory by supposing that rapid rotation helps to dissolve the film. The solubility of the film (disappearance of passivity) is very rapid when iron is made passive by electrolysis in sulphuric acid. The solubility in nitric acid must also be an important factor.

This experiment also shows the futility of trying to present convincing arguments in favor of any theory in regard to this question without giving all the conditions of the experiment in fullest detail.

Since the publication of the advance copy of this paper I have tried to verify this experiment of rotation, but without success. Even with rapid rotation I found that iron in 1.40 nitric acid always became passive.

I used the "potential test" for passivity, which is much more reliable than the "Heathcote" test presumably used by the authors. The latter test is very indefinite, in that the iron to be tested is shaken in dilute nitric acid for a moment (how long is a moment?) and then chemical action at the surface is detected by the eye. In my experience the time of beginning of chemical action is extremely difficult to judge by the eye—depending very much on previous polish of the surface, and light conditions. Any passive iron will become active in dilute nitric acid in a comparatively short time.

Irving Langmuir: It seems to me that the essentially new element in this paper of Bennett and Burnham is the idea that the film which causes passivity is stabilized by adsorption. I

think this idea marks a distinct advance over previous work on passivity. Until we have more definite ideas as to the meaning of stabilization by adsorption, however, there is little justification for the statement in the paper that "according to this view all the facts of passivity are easily explained."

The theories of passivity have been manifold, as we all know, and the subject does not seem to get clearer as time goes on. What we need is a new viewpoint which will lead us to an understanding of the mechanism and kinetics, not only of passivity, but of all surface phenomena, among which passivity, overvoltage, adsorption, catalysis, electron emission, and many others are but special cases.

During the last few years I have been endeavoring to develop such a viewpoint in connection with a study of the surface phenomena involved in chemical reactions between solids and gases at low pressures. Some of this work seems to have a very direct bearing on the phenomena of passivity. In fact we have frequently observed unmistakable passivity phenomena in these gas reactions, and I feel sure that we have the proper explanation of them. The theory that applies to these reactions seems capable of extension to the field of electrochemical phenomena.

I will describe to you briefly one of these cases of passivity in gas reactions. If oxygen at low pressure be introduced into a bulb containing a tungsten filament heated to 1500° K. (absolute), the oxygen will gradually react with the tungsten to form the trioxide, WO_3, which distils from the filament onto the bulb as fast as it is formed (Journal Amer. Chem. Soc. (1913) **35**, 105). The pressure of the oxygen in the bulb thus decreases at a rate proportional to the pressure, as indicated by curve I (see Fig. 1).

If instead of oxygen, hydrogen at low pressures be introduced into the bulb, the hydrogen gradually disappears at a rate not greatly different from that observed with oxygen. (Curve I.) It has been found that this is due to the dissociation of the hydrogen into atoms and the adsorption of the atomic hydrogen on the glass walls of the bulb (Jour. Chem. Soc. (1912) **34**, 1310).

When oxygen and hydrogen are admitted together into the bulb and thus come into contact with the highly heated filament, we might expect that they would react together to form water.

Instead of that, we find that the oxygen reacts with the tungsten to form WO_3, just as though no hydrogen were present. Careful experiments show that no appreciable portion of the WO_3 is reduced by the hydrogen under these conditions, although at atmospheric pressure this oxide is readily reduced by hydrogen at 500° C. After practically every trace of the oxygen has been consumed, the hydrogen suddenly begins to be dissociated, and then gradually disappears at the same rate as though no oxygen had been present. The way in which the pressure decreases when both oxygen and hydrogen are present is shown by curve II (see Fig. 1).

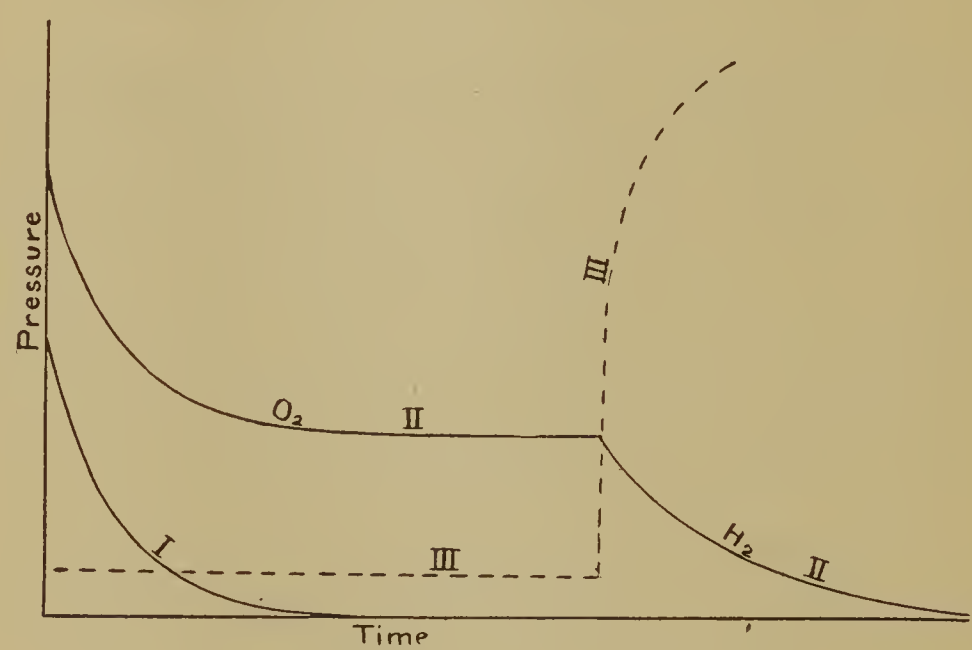

FIG. 1.

The presence of very minute traces of oxygen (calculation shows that a pressure as low as 10^{-9} mm. of mercury is effective) thus completely prevents any hydrogen from being dissociated in contact with the heated wire. When the oxygen has been practically completely consumed, then the dissociation begins suddenly. This is a clear case of passivity. The oxygen renders the tungsten passive.

When a tungsten filament is heated in a high vacuum it gives off electrons. By placing a positively charged electrode in the bulb and connecting this through a galvanometer, the current produced by this emission of electrons may be measured. It has been previously found that traces of oxygen enormously decrease the electron emission from tungsten (Phys. Rev. (1913) **2**, 450), whereas hydrogen has no effect. If the electron emission is meas-

ured while a mixture of oxygen and hydrogen is in the bulb, the current is found to vary as indicated in curve III (see Fig. 1). The electron emission thus undergoes a sudden increase at the same instant that the chemical passivity disappears.

These and many other phenomena are satisfactorily explained if we assume that in the presence of oxygen the surface of the tungsten is completely covered with a layer of oxygen atoms chemically combined with the tungsten atoms forming the surface layer. These tungsten atoms are held by chemical forces to the underlying tungsten atoms and these in turn to the next layer and so on throughout the mass of the filament (Bragg's crystal structure). Thus the oxygen is chemically saturated by being combined with the tungsten, but the tungsten is not saturated by the oxygen. The oxygen being chemically saturated and having its chemical forces directed downwards towards the tungsten, has practically no tendency to combine with hydrogen. When, however, the oxide film distils off, and the supply of oxygen by which it could be replenished is used up, then the hydrogen molecules for the first time come into contact with the bare tungsten surface and are afforded an opportunity of being dissociated.

The layer of oxygen atoms on the surface of the tungsten constitutes an adsorbed film, in which, as Dr. Bancroft would say, the oxygen is stabilized by adsorption. The film, however, does not consist of adsorbed oxide, nor adsorbed gas. The oxygen is evidently in the solid condition, since it forms a continuation of the space lattice of the tungsten crystal.

The work of Bragg has conclusively shown that the *atoms* of crystals are arranged in definite lattice-like structures, in which the identity of the molecules is usually lost. In the case of sodium chloride each sodium atom is surrounded by six chlorine atoms equidistant from it.

Evidently the forces which hold the crystal together are chemical forces. In the case of metallic iron the atoms are similarly arranged, and we must assume that the crystals of iron are held together by chemical force. These forces are very great. The latent heat of evaporation of a substance is a measure of the attractive forces between its atoms. Recent work has shown that the latent heat of evaporation of iron is about 80,000 calories per gram atom—a quantity larger than the heat of combustion

of hydrogen. The chemical forces holding iron atoms together are thus very great. Each atom inside a crystal of iron is probably surrounded by twelve other equidistant from it. The forces acting on each atom are balanced against one another.

The atoms on the surface of a crystal have only from four to eight neighbors, so that the forces must be very much unbalanced. We should therefore expect these atoms to be unsaturated chemically and to exert strong attractive forces on any atoms coming close to the surface.

When a piece of clean iron is placed in water it is practically certain that the iron atoms on the surface will combine chemically with the various kinds of atoms and molecules in the water, without, however, losing their chemical attraction for the underlying atoms of iron. The surface of the iron thus becomes completely covered with an adsorbed film which probably consists of atoms of both hydrogen and oxygen (and possibly hydroxyl radicals).

Now in the gas reactions that I have studied the adsorbed films are usually in dynamic equilibrium with the surrounding gases. That is, the atoms in the film are continually distilling off, while other atoms or molecules in the gas are condensing on the surface to take their places. In the case of the tungsten filament in a mixture of oxygen and hydrogen, the essential difference between the oxygen and the hydrogen is that the oxygen atoms distil off a tungsten surface very much more slowly than the hydrogen atoms. This is the real cause of the passivity of the tungsten.

In a similar manner we may account for the passivity of iron. Thus hydrogen atoms on the surface are continually passing back and forth between the surface of the metal and the solution, whereas oxygen atoms are so firmly held by the metal that they are rarely displaced.

In the presence of oxidizing agents the whole surface of the iron becomes covered with adsorbed oxygen atoms which protect the iron from attack. If this layer is removed by reducing agents, the surface becomes largely covered by hydrogen (or hydroxyl) and because of the comparatively high mobility of these, the surface is continually exposed to attack. (A very brief outline of this theory was published in the Physical Review (1915), **6**, 79).

The various theories of passivity that have been proposed may be divided roughly into:

1. The oxide film theory of Faraday.
2. The oxygen theory (Fredenhagen, etc.).
3. The hydrogen theory (Foerster and Schmidt).
4. The reaction velocity theory (Le Blanc).
5. Anion discharge theory (Sackur).
6. Reichinstein's constant sum theory.

The theory which I have outlined above does not come under any one of these headings, but it seems to combine and reconcile them all.

Thus, since practically the whole surface of the iron is covered with an adsorbed film of some kind all the time, hydrogen must be present when oxygen is absent. The distinction between the oxygen and the hydrogen theories thus disappears. Since the extent of the surface covered by oxygen depends upon the relative mobilities of the oxygen and hydrogen, Le Blanc's reaction velocity theory finds application. The velocity with which the iron is attacked depends on the facility with which the discharged anions can come into contact with oxygen-free surface, so that the theory seems to be in accord with the essential elements of Sackur's theory. Finally, the fact that the sum of the surface areas covered by hydrogen and oxygen respectively must always be approximately equal to the whole surface, is in full accord with Reichinstein's little-understood constant sum theory, which states that "The sum of the concentrations of all the constituents of the 'electrode volume' is always constant."

I hope soon to apply this theory quantitatively to actual experimental data on passivity.

N. K. Chaney: May I ask how the "electrode volume" would come in, or does he attribute that to the porosity of the electrode film?

Irving Langmuir: The "electrode volume" is simply an hypothesis of Reichinstein's to account for the possibility of displacement of one substance by another. Reichinstein found experimentally certain results which led him to conclude that the sum total of all the concentrations at this surface must be constant, and therefore he talked about concentration. If you substitute

for "concentration" the idea of the extent to which a surface is covered with atoms, then, instead of the sum of the concentration being constant, you say the total sum of the space on the surface is constant. You then get Reichinstein's hypothesis in different language, and you can then talk about the "electrode volume" as the electrode surface.

C. W. Bennett: We have referred to the Faraday or oxygen theory. Faraday was canny in his statement, brief as it was, covering the oxygen theory. We have to ascribe to Faraday both the oxygen and the oxide theory. However, if the oxygen theory had not been worked out later, we would scarcely have discovered the oxygen theory in what Faraday said.

With reference to the oxygen theory mentioned by Mr. Chaney, that is not, of course, included in the paper itself. A piece of iron when dipped in nitric acid, removed and allowed to dry in air, is very tenacious of its passivity. Mr. Chaney has shown that in the case of zinc electrodes acquiring a film of hydrogen, presumably upon lifting them out of the electrolyte and exposing them to air, causes them to lose that film of gas. If passivity is due to an oxygen film, passive metal should lose the film of oxygen to some extent, by lifting it out and placing it in air. That is, part of the oxygen should be replaced by nitrogen, if it is oxygen, and the iron should not be so persistently passive as it was before drying. As a matter of fact we know that it is more passive, more noble, after being exposed to air and dried than it was before, so that that constitutes a very weighty argument against any oxygen film. Any oxygen film on the surface, explaining passivity, would not explain the different results obtained with chromium and with iron. Chromium dissolves as hexavalent ion in certain solutions and as divalent ion in others.

Without the assumption of a definite oxide, I do not see how we can explain the solution of chromium in this way. Iron, of course, dissolves only very slowly, and not with any reasonable valence when made anode in oxidizing solutions. One forms a soluble oxide and the other forms an insoluble oxide, thereby explaining the different behavior in the two cases, while if we assume an oxygen film we could not explain this different behavior in any way.

Referring to the experiment of rotating the iron rod in a chuck, this was performed by Mr. Burnham and I was not present. The chuck was probably rotated 2,500 to 3,000 r. p. m., and if I remember correctly he raised the beaker slowly on the rod while it was rotating. If you put the rod in the acid and begin the rotation, it is probable it would not become passive, because hydrogen would be liberated very rapidly at the surface and the potential would be lowered.

Referring also to the definite break in the potential current curve while making iron passive, I would point out the fact that in repeatedly making a piece of metal passive, you never obtain the break at the same point. This probably represents the coating of the surface and this represents the oxygen polarization, that is, the voltage-time curve with constant current. We have to consider active iron, then iron with the surface partially coated with an adsorbed film, finally becoming completely coated, and then the iron acting as a passive or inert electrode or essentially as an oxygen electrode.

One of the serious difficulties of Mr. Langmuir's theory is that if passive iron is coated with a molecular film of oxide, hydride, or oxygen in solid solution, the facts of passivity are not explained. I will mention only one case to support this contention. Take a piece of iron and make it passive by dipping in concentrated nitric acid, then place it in 1.20 nitric acid, which is used by Heathcote for testing the passivity. Suppose we take an iron rod and make it passive on a portion of its surface. If we place it in the 1.20 acid to the limit of passivity, the rod does not dissolve for several minutes. If we lower the rod farther in the acid, the newly-immersed portion does not become active, that is, we can extend the passivity over a considerably larger surface than the original surface by lowering the rod.

I can see no reason, therefore, why, when we stretch this passivity over practically 150 or 200 percent of the original surface, the iron would not be bared in some spots; that is, if we have a molecular film over the surface and spread this out into half a molecular film, we could not have the passivity which we know we do have. So, an attempt to explain passivity by molecular films is absurd, because you cannot stretch these films to half molecular thickness, since such can not exist.

It appears to me we will have to go back to a film of reasonable thickness, which will protect the metal, and the amount of protection depends on the thickness of the film. That is, if you have the film very thick you can make twice the original surface passive by lowering the rod gradually into the acid.

Mr. Langmuir says that passive iron is inert, that is, that this film would make the iron inert. I do not think he meant it in just that way. Passive iron is not inert but extremely active, because it develops a high potential. That is, the oxide will react, and depolarize hydrogen, and therefore it is not inert in the strict sense of the word. It is inert from the standpoint of the solution of the iron, but even according to his theory we are not dealing with iron, but with a film over the surface.

It is a waste of time to pursue such a fanciful hypothesis further, since it is evident that the author has not tried to explain any of the facts of passivity by applying it. Any sort of slowly-dissolving film would slow down the solution of a metal in acid. A coating of shellac protects iron from attack by acid, but none of the facts of true passivity are explained by such a phenomenon.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

OVERVOLTAGE.

By C. W. Bennett and J. G. Thompson.

A large number of measurements of overvoltage have been made and the phenomenon has been characterized many times as very complex. The unsatisfactory state of the published knowledge of the subject may be seen by a consideration of a few of the definitions and theories of overvoltage. The cathode decomposition voltage of sulphuric acid solution with a platinized platinum cathode is a definite value. This value is different if smooth platinum or a zinc cathode be used. These values will all differ, depending on whether the voltage drop at the electrode is measured as the voltage is increased, or whether the back electromotive force of polarization is measured.

Overvoltage has been defined in several ways. Caspari[1] considers hydrogen overvoltage, for instance, as the difference between the voltage at a platinized cathode when bubbles of hydrogen form, and at the metal in question under the same conditions. In other words it is the difference in the voltages required to liberate hydrogen at the surfaces of the two metals under the same conditions.[2]

Values for overvoltages of hydrogen and oxygen at several metal electrodes are given in Table I.

The values differ depending on whether the point of gas evolution or whether the break in the voltage current curve is taken. The values also increase with an increase of current density. Le Blanc[5] considers the phenomenon from the standpoint of the electromotive force of the cell after the charging circuit is broken. He considers hydrogen overvoltage as the excess back electromotive force generated at the electrode over that at a platinized

[1] Zeit. phys. Chem., **30**, 89 (1899).
See also Coehn and Dannenberg: *Ibid.*, **38**, 618 (1901).
[2] See Fuchs: Pogg. Ann., **156**, 156 (1875).
[5] Text-book of Electrochemistry.

platinum electrode. This may be obtained by rapidly closing the charging circuit and as rapidly breaking it, making a new circuit through suitable measuring instruments. This is accomplished by a commutator rotating 1200-1500 revolutions per minute[6].

It is evident, therefore that the phenomenon has been considered from the relative standpoint of an arbitrary standard. The significance of this is realized when it is considered that palladium has a "negative overvoltage," which all but gives the impression, especially to the beginner, that there is a gain in the energy of the system when hydrogen is set free at the surface of a palladium electrode.

TABLE I.

Hydrogen and Oxygen Overvoltages.

Electrode Material	Overvoltage (Volt) according to				
	Caspari		Müller[3]	Coehn and Dannenberg	Thiel and Bruening[4]
	Hydrogen	Oxygen	Hydrogen	Hydrogen	Hydrogen
Pt. platinized	0.005	0.39	0.01	0.0	0.0
Palladium	0.46	0.39	0.24	—0.26	0.0
Pt., polished	0.09	0.62	0.07	.....	....
Gold	0.02	0.59	0.06	+0.05	0.016
Silver	0.15	...	0.05	+0.07	0.097
Copper	0.23	...	0.03	+0.19	0.135
Nickel	0.21	...	0.03	+0.14	0.138
Retort carbon.....	...	...	...	.....	0.143
Iron	...	...	...	+0.03	0.175
Iron in NaOH....	0.08	...	...	.....	0.087
Graphite	...	...	...	.....	0.335
Cadmium	0.48	...	...	.....	....
Tin	0.53	...	0.43	.....	....
Lead	0.64	...	0.35	+0.36	....
Zinc	0.70	...	...	.....	....
Mercury	0.78	...	0.42(?)	+0.44	....
Aluminum	...	...	...	+0.27	....

[3] Müller: Zeit. anorg. Chem., **26**, 56 (1901).
[4] Thiel and Bruening: *Ibid.*, **83**, 329 (1913).

A new definition of overvoltage will include not only hydrogen, oxygen, and other gases, but also the metals, for the latter have definite overvoltages. It is evident that the definitions of overvoltage in use at the present time are not general, since they, none of them, apply to metal overvoltage.

[6] See LeBlanc: Zeit. phys. Chem., **5**, 469 (1890).

Throughout this discussion, therefore, the term overvoltage will be used in the general sense and will denote the excess back electromotive force of the system (cathode or anode as the case may be) under investigation, over the electromotive force of the system consisting of the final product obtained (at anode or cathode) in the solution used.

The overvoltage of hydrogen at a metal electrode would be the excess of the back electromotive force of the metal cathode (containing hydrogen) during electrolysis, over the electromotive force of the reaction

Hydrogen gas → dissolved hydrogen ion.

This overvoltage varies with the metal used because the metals act differently towards hydrogen. The overvoltage of a metal, zinc, for instance, would likewise be the excess of the back electromotive force of the system:

Zinc → zinc solution during electrolysis

over the electromotive force of the reaction

Solid zinc → dissolved zinc ion.

The overvoltage therefore represents the excess energy required to form a substance over that given by the re-solution of the product formed to the original state. It is the amount of energy by which one measures the irreversibility of the process or change.

A number of theories have been suggested to explain overvoltage.

Haber[7] assumed that the electrode adsorbs a film of gas and that the resistance is increased. This is not worthy of consideration when it is realized that a resistance at the electrode would lower the electromotive force of the polarized cell, and also that metals while being deposited have definite overvoltages which must be considered aside from any gas formation.

Nernst[8] ascribed the cause to the slowness with which the electrode gets into equilibrium with the surrounding atmosphere. He considers that before the gas can be liberated the ions must be

[7] Haber: Zeit. Elektrochemie, 8, 539 (1902).
Haber and Russ: Zeit. phys. Chem., 47, 257 (1904).
[8] Theoretical Chemistry, 766 (1911).

driven into the electrode. Metals which have only a slight tendency to occlude gases, require energy to force the gas into the electrode, and thus give high overvoltages.

Möller[9] considers that the overvoltage is the energy necessary to give a film of gas thick enough to generate bubbles.

Foerster[10] claims that at a platinum anode, an oxide, probably PtO_3 is formed. This as a solid solution would generate a high back electromotive force, and therefore give a high oxygen overvoltage at a platinum anode. In the case of the other metals where the higher oxide is unstable, it would not accumulate in appreciable quantities and hence the overvoltage would be low. Hydrogen overvoltage would be explained by the assumption of the formation of a solid solution of hydride probably. This theory does not satisfactorily explain the overvoltage of metals.

Tafel[11] takes a view similar to Nernst, in that he considers the forcing of the gas into the electrode takes time, and the excess gas accumulated generates the back electromotive force. He also considers that in the case of hydrogen an intermediate state exists between dissolved ion and gaseous hydrogen. This monatomic hydrogen forms free hydrogen, more or less rapidly, depending on the catalytic effect of the metal of the electrode. When the reaction is slow and the concentration of the intermediate product high, the overvoltage is high and *vice versa.*

This theory was suggested by Ostwald[12] previous to this as a possible explanation and also by E. Müller.[13] This view was accepted by Lewis and Jackson.[14] They say: "The theory of overvoltage, with which the authors began these experiments, was as follows: The reaction, $2H^+ + 2\theta = H_2$, does not occur in a single stage, but in the two following: $H^+ + \theta = H$, and $2H = H_2$. The reaction whose slowness causes the polarization is the second of these. In other words, the potential of a hydrogen electrode depends on the concentration of monatomic hydrogen, and this concentration increases rapidly during cathodic

[9] Drude's Ann., **25**, 725 (1908).
Zeit. phys. Chem., **65**, 226 (1908).
[10] Zeit. Elektrochemie, **16**, 353 (1910); Zeit. phys. Chem., **69**, 236 (1909).
[11] Zeit. phys. Chem., **34**, 200 (1900).
Ibid., **50**, 641, 713 (1905).
See also Brunner: *Ibid.*, **56**, 331 (1906).
[12] Zeit. Elektrochemie, **6**, 40 (1899).
[13] Zeit. anorg. Chemie, **26**, 11 (1901).
[14] Proc. Am. Acad., **41**, 399 (1906).
Zeit. phys. Chem., **56**, 207 (1906).

polarization on account of the slowness of the reaction by which it is removed. For example, at a polarization potential of 0.7 volt the concentration of this substance at the electrode would be 10^{12} times as great as it would be when in equilibrium with ordinary hydrogen. Nevertheless both of these concentrations might be absolutely very small, and probably are. The difference in polarization with different cathodes would be explained by the different catalytic action of the material at the electrode, the polarization being less the greater the catalysis. This theory, although it has been suggested by Tafel,[15] has had otherwise no place in the numerous discussions which the phenomenon of overvoltage has occasioned. It possesses, nevertheless, a good deal of plausibility. We may in fact cause the electrolytic reaction to proceed in the very two stages which we have written above. When hydrogen is deposited on a palladium cathode, the hydrogen, forming without marked polarization, is absorbed by the metal, where it has been shown by two independent methods[16] to exist in the monatomic condition. If the hydrogen is then withdrawn from the palladium, it appears in the form of ordinary hydrogen, H_2.

"But we have more striking arguments in favor of this theory. Those metals, notably platinum and palladium, in whose presence the electrolytic deposition of hydrogen and the reverse reaction, the electrolytic solution of hydrogen progress most readily, are the very ones which we have every reason to believe catalyze the raction $2H \leftrightharpoons H_2$ (of course, if in one direction, in both). This reaction is doubtless a very slow one under most conditions. Hydrogen at ordinary temperatures is a pretty inert substance, but in the presence of palladium or platinum black it readily reduces a large number of substances. So, also these metals aid the union of hydrogen with other elements, such as oxygen and the halogens. Furthermore, in every known case where hydrogen is produced by a reaction, the reaction is catalyzed by these metals. We may mention the action of metals on acids, the reduction of water by chromous salts, the decomposition of a solution of sodium in liquid ammonia.[17] It is possible that each of

[15] Zeit. phys. Chem., **34**, 200 (1900).
[16] Hoitsema: Zeit. phys. Chem., **17**, 1 (1895).
Winkelmann: Drude's Ann., **6**, 104 (1901).
[17] The interesting fact that this latter reaction is greatly accelerated by platinum was brought to our notice by Dr. C. A. Kraus.

these reactions is catalyzed in a specific way; but it is much easier to believe that in every case the metal simply catalyzes the slow reaction, $2H \leftrightharpoons H_2$, and that this is also the explanation of the electrolytic reaction that we are considering. It is to be noted that metals like mercury and lead, on which the overvoltage is highest—that is, which are the poorest catalyzers of the electrolytic reaction—have little influence on any of the reactions mentioned above.

"Although we have laid stress upon the *a priori* plausibility of this explanation, we are nevertheless forced to admit that while our experiments are in no way opposed to the theory, they fail at the same time to give any evidence in its favor, except in so far as they enable us to exclude certain other explanations and thus limit the field of possibilities. If the main reaction at the basis of polarization is the formation of ordinary hydrogen from monatomic, then our experiments only show that this reaction does not occur in a single homogeneous phase. Since in all probability the monatomic hydrogen is present in extremely small concentration, this would account for the slowness of any diffusion process in which it enters, even if the diffusion were through a thin film."

Bose[18] considers also that the neutral gas may have its influence in that ions may be formed from it.

Le Blanc[19] assumes that as the ion is discharged the following reaction occurs

$$\text{ion hydrate} \leftrightharpoons \text{ion} + \text{water}.$$

An equilibrium exists in the solution, and when the ion is set free, this is displaced and polarization is set up, giving back electromotive forces of different magnitudes, depending on the ions used. Overvoltage occurs when the reaction above from left to right is slow.

Reichinstein[20] also considers that the ions as well as the gas formed penetrate the electrode. When this penetration is great, the overvoltage is small, for the electromotive force is low due

[18] Zeit. phys. Chem., **34**, 701 (1900).

[19] Abhandlungen d. deutschen Bunsen Gesell. No. 3 (1910), Knapp. Trans. Faraday Soc., **9**, 253 (1914).

[20] Zeit. Elektrochemie, **15**, 734, 913 (1909); **16**, 916 (1910); **17**, 85 (1911); **18**, 850 (1912); **19**, 672 (1913). Trans. Far. Soc., **9**, 229 (1914).

to low concentration. When the "electrode volume" is small the overvoltage is high, due to high concentration of the ions in the electrode.

The above review presents probably the best known theories for the explanation of the phenomenon. However Newbery[21] concludes that overvoltage is determined by three factors: first, the metal is permeable to electrified gas, leaving the surface supersaturated with non-electrified gas under high pressure; second, at this surface there may be metastable intermediate products (probably non-hydrated ions) either in deficiency or excess; and lastly, the gas evolved exerts an inductive effect on the electrode.

The striking feature of these theories is that those which are intelligible are obviously inadequate.[22] Not one will explain metal overvoltages, for instance. The majority of the explanations, however, are unintelligible when it comes to a consideration of the exact mechanism of the reactions.

In view of the fact that several of these theories embody threads of evidence pointing to the explanation of certain parts of the general proposition, it is expedient that the several ideas be gathered up and unified into a general theory of overvoltage, which explains overvoltages of gases at metal electrodes as well as overvoltage of metals. A discussion of this interesting phenomenon is especially opportune, now that there need be no postulation of the existence of hypothetical intermediate products in the case of the gases. The intermediate products have not only been isolated, but have been found to possess just the necessary properties to be used in the case at hand.

Let us consider some of the known facts concerning hydrogen. The reaction

$$\text{Hydrogen ion} \rightarrow \text{hydrogen gas}$$

[21] Jour. Chem. Soc., **105**, 2419 (1914).
[22] For other papers on overvoltage, see
Kaufler: Zeit. Elektrochemie, **13**, 635 (1907); **14**, 321, 737, 749 (1908).
Müller: *Ibid.*, **13**, 681 (1907).
Sacerdoti: *Ibid.*, **17**, 473 (1911).
Nutton and Law: Trans. Far. Soc., **3**, 50 (1907).
Pring and Curzon: *Ibid.*, **7**, 237 (1912).
Pring: Zeit. Elektrochemie, **19**, 255 (1913).
Thiel and Bruening: Zeit. anorg. Chem., **83**, 329 (1913).
Crabtree: Trans. Far. Soc., **9**, 125 (1913).
Jour. Soc. Chem. Ind., **32**, 521 (1913).
Richards: Trans. Far. Soc., **9**, 140 (1913).

is not strictly a reversible one, for it is known that "nascent hydrogen" or hydrogen produced when the above reaction proceeds will perform reductions, which do not go on even in the minutest measurable amount when hydrogen gas is bubbled through a similar solution containing the substance to be reduced. Hydrogen gas even when dissolved is inert.[23] Hydrogen will not reduce hydrogen peroxide or ozone spontaneously when cold, although both of these substances will be decomposed by "nascent hydrogen." It is evident, therefore, that the condition of hydrogen, intermediate between gas and dissolved ion, is many times more active than hydrogen gas (H_2). This form must be a stronger reducing agent than H_2 and probably even stronger than zinc itself. It will be shown below that this "active hydrogen" will reduce phosphorus, zinc oxide, and cadmium sulphate, which will indicate that it is a stronger reducing agent than zinc.

The existence of an intermediate stage, more reactive than either of the end products, is a condition of every day acquaintance. For instance, sodium hypochlorite and sodium chlorate solution will oxidize ferrous salts, but neither sodium chloride nor sodium perchlorate solutions will effect the oxidation. The intermediate products are less stable and more reactive than the end products. Theoretically and practically such a condition is possible.[24] The case of ammonium hydroxide, hydrazine hydrate and hydroxylamine, or ammonia, hydrazine, and hydronitric acid as reducing agents, as well as many others, present themselves.

The active form of hydrogen is produced at the cathode during electrolysis of an acid, during solution of a metal in acid (more active with metals like zinc), by the action of radium emanations (for these form hydrogen, oxygen, and hydrogen dioxide from water), and lastly, by the action of electrical discharges or by photochemical effects. An extremely active modification of hydrogen has lately been prepared and designated.[25] When a tungsten or platinum wire is heated from 1,200°-3,500° absolute, in an atmosphere of hydrogen at very low pressures, the hydrogen disappears, and when the containing glass bulb is cooled

[23] See Sackur: Zeit. phys. Chem., **54**, 641 (1906); Weigert: *Ibid.*, **60**, 543 (1907).
[24] Luther: Zeit. phys. Chem., **34**, 488 (1900); **36**, 385 (1901).
[25] Langmuir: Jour. Am. Chem. Soc., **34**, 860, 1310 (1912).
Freeman: *Ibid.*, **35**, 931 (1913).
Langmuir and Mackay: *Ibid.*, **36**, 1708 (1914).
Langmuir: *Ibid.*, **37**, 417 (1915).

in liquid air there is condensed on its surface atomic hydrogen (H) which may be kept in this active state for several days. When the bulb is heated and the wire cooled, the hydrogen reappears and the active material is not recondensed until the wire or filament is reheated. This active hydrogen will reduce phosphorus even at room temperature, with the formation of phosphorus hydride. The explanation is given that hydrogen dissolves in the hot metal, dissociates, and on being driven out, passes directly to the walls of the container where it may be condensed. It is neutral, that is, it is not electrically charged, for it is not attracted or deflected by electrostatic fields. The quantity or amount of dissociation at 760 mm. pressure is shown in the following table where

$$K = \frac{P_1^2}{P_2}$$

in which P_1 is the partial pressure of hydrogen atoms (H) and P_2 that of hydrogen gas (H_2).

Temp. Abs.	K
2,000°	0.0033
2,300°	0.0140
2,500°	0.0310
3,100°	0.1700
3,500°	0.3400

Supplementing the work of Langmuir on the properties of this active material one or two experiments may be given. A filament of molybdenum wire was heated close to the volatilization point in a current of hydrogen over solutions of copper, zinc, and cadmium sulphates. In one case a small amount of copper was obtained, while in a number of cases the cadmium solutions yielded precipitates which after thorough washing gave microscopic tests for cadmium with ammonium mercuric sulphocyanate. This shows that at the temperature used the hydrogen was sufficiently activated to reduce small quantities of cadmium from cadmium sulphate solution.

Another experiment was tried in which ultra-violet light was used to activate the hydrogen. The gas was passed through a quartz tube which held a glass slide, on the side toward the light painted with a paste of zinc oxide and water. A Macbeth printing lamp was used as the source of ultra-violet light. The sur-

face of the paste was readily blackened on exposure to the light. The hydrogen used was first electrolytic hydrogen and finally hydrogen generated by the reaction of sulphuric acid and zinc. It was found that the electrolytic hydrogen produced no blackening in the dark or in the daylight, but produced a blackening due to the reduction of the zinc oxide[26] when exposed to the action of ultra-violet light. A difference in the action of hydrogen generated by zinc and sulphuric acid was found, but this was later shown to be due to impurities in the chemically generated hydrogen. The active hydrogen is sufficiently active to reduce zinc oxide.

The zinc oxide paste slide was exposed to the action of a stream of hydrogen by having a glazed paper placed between it and the source of ultra-violet light. The light, therefore, passed through the hydrogen and this hydrogen later reached the glass slide. It was found that the blackening was most marked at the end next to the incoming hydrogen, and was distinct even after the hydrogen had passed two centimeters from the point of activation. The blackening effect on the slide was graduated from the incoming end, fading out gradually as the hydrogen passed over toward the outlet. This shows without question that active hydrogen will reduce zinc oxide, and that it has a definite period of life, depending upon the conditions under which it exists.

Analogous to hydrogen, oxygen (O_2) is formed from the dissolved ion irreversibly,[27]—nascent oxygen produced by electrolysis, or photochemically, will oxidize substances which are unacted upon by hydrogen dioxide or ozone.

Active oxygen (presumably O_1) and active chlorine have been prepared[28] by heating oxygen and chlorine under low pressures, with a tungsten or platinum filament. Active oxygen may be condensed by liquid air, and even at that temperature reacts readily with tungsten. Active chlorine may be condensed in the same way. It is also very active.

It may be said, therefore, with all certainty, that these reactive products exist, intermediate between free gaseous molecules and

[26] O'Brien: Jour. Phys. Chem., **19**, 130 (1915).
[27] See Coehn and Osaka: Zeit. anorg. Chem., **34**, 86 (1903).
[28] Langmuir: J. Am. Chem. Soc., **37**, 1162 (1915).
See also
Bredig and Weinmayr: Z. phys. Chem., **42**, 607 (1903).
J. Am. Chem. Soc., **35**, 105, 931 (1913).

dissolved ions. Take the specific case of hydrogen, for instance. When hydrogen (H_2) dissolves in a solution, the first step is to form H_1 neutral. The next step is the formation of H_1, dissolved ion. Hydrogen gas can ionize only through such a series of changes.

A consideration of these reactions in opposite directions will indicate why they are not reversible, statements to the contrary notwithstanding.[29] As hydrogen gas dissolves, it becomes ionized. The concentration of H_1 goes from zero to a maximum value, namely, the equilibrium concentration. Since energy is not added from without, this equilibrium concentration practically cannot be exceeded, otherwise the reaction would reverse. Any variation from this will be in the direction of a lower concentration. Considered from the other side, now, where energy is added, the first step is the formation of H_1 from $\dot{H}_1$, dissolved ion. Then gas (H_2) is formed. The same equilibrium exists here as before, but gas is formed only when the equilibrium concentration of H_1 is exceeded, otherwise the reaction would stop or reverse. The reaction where hydrogen dissolves, becoming ionized through the intermediate stage, is connected with the formation of active hydrogen (H_1) in equilibrium concentration, while the reverse reaction forms active hydrogen (H_1) in concentrations from equilibrium up to values depending on the conditions of the electrolysis. This difference, which will depend on the conditions, is a true measure of the irreversibility of the process.

From the standpoint of the transformation of chemical energy into electricity, the irreversibility becomes even more evident. Hydrogen as H_2 ionizes through this series of reactions,

$$H_2 \text{ dissociates} \rightarrow 2H_1, \text{ assumes charge} \rightarrow 2\dot{H}.$$

This reaction generates a certain quantity of electricity with a definite intensity, the product of which represents the total chemical energy. In the reverse direction hydrogen gas is not formed until equilibrium is reached or at higher concentrations of active hydrogen if the conditions are not conducive to carrying out the

[29] Neumann: Zeit. phys. Chem., **14**, 203 (1894).
Westhaver: *Ibid.*, **51**, 65 (1905).
Lewis: Jour. Am. Chem. Soc., **28**, 160 (1906).
Haber: *l. c.*

reaction, $2H_1 \rightarrow H_2$, quickly. When equilibrium is exceeded, at any rate, energy of greater intensity must be required to carry on the reaction. The total voltage or back electromotive force is that occasioned by the active hydrogen present. The excess back electromotive force or overvoltage is that occasioned by the active hydrogen present in excess of equilibrium concentration. The energy required to form this excess active hydrogen is equal, with a change of sign, to the energy yielded by the decomposition of the excess active hydrogen to form gaseous hydrogen. The latter has been calculated and will be mentioned below. The process is irreversible, therefore, by the energy, or heat, of formation of active hydrogen in such concentration as it is present above equilibrium.

The process of solution and deposition of a metal cannot be considered reversible. Consider the electro-deposition from solution. The first step is the loss of a positive charge from the ion. This will result in the formation of free atomic metal, in the case of monovalent ions. Suppose we consider the case of zinc without assuming a monovalent zinc ion. The divalent ion becomes free atomic material. Its condition is the same as that of zinc in the vapor state. Zinc vapor, according to vapor density measurements, is Zn. When the ion in solution loses the charge it becomes Zn, and therefore it must be analogous to the vapor, the difference being that the zinc atoms (Zn_1) can come closer together on account of the lower temperature. Analogous to hydrogen when the concentration of Zn exceeds equilibrium values, a complex Zn_x will be formed. In other words the material will go into a condition analogous to a "melt",[30] and from this it will crystallize.[31] Equilibrium concentration value must be exceeded at each stage else the reaction would come to a standstill or reverse. Consider the reverse reaction. Crystalline metal breaks down to complexes which then dissociate to Zn_1 which goes into solution with the assumption of two positive charges of electricity. During this change equilibrium concentrations are never exceeded. If they were the reaction would reverse.

[30] Reichinstein: Zeit. Elektrochemie, **17**, 89 (1911).
Bennett: Trans. Am. Electrochem. Soc., **21**, 256 (1912).

[31] Cf. Ostwald: Trans. Am. Electrochem. Soc., **6**, II, 194 (1904).

Considering the two reactions as proceeding continuously, with zinc of the same crystal structure in both cases, one reaction forms Zn_1 in concentrations up to, and the other above, equilibrium values. This measures the irreversibility of the process.

Zn_1 represents energy of greater intensity than the crystalline zinc, for it has been shown conclusively that the solution pressure, and therefore the voltage varies inversely with the size of the crystals.[32] Zn_1 may be considered as the last stage in the decrease in the size of the crystals or particles of zinc. This consideration shows that more energy will be required to deposit zinc from solution, than is yielded by its re-solution and the process is irreversible in that sense.

Suppose we consider the case where ions of intermediate valency may be formed. Copper, for instance, is deposited from copper sulphate solution with the formation of some cuprous ions. This reaction may be irreversible by an amount depending on the quantity of cuprous ions formed and reoxidized either by air or at the anode. It has been shown that copper deposition from copper sulphate solution requires a higher voltage the more rapidly the cathode is rotated.[33] This is higher than that required for a stationary cathode, even though the solution is stirred vigorously. This was shown to be due to the formation of cuprous ions and their removal by rotation from the cathode solution film before they can be reduced to copper.[34] Thus the concentration of cuprous ion is kept at practically zero, with a consequent strong tendency to form them. This process, however, is probably reversible, for the solution of copper in copper sulphate generates a higher voltage when the copper is rotated, the voltage increasing with rotation. This formation of ions of intermediate valency in concentrations above equilibrium differs from the cases considered above in that the intermediate ions are in the solution film, while the free intermediate atoms are in the electrode film. The former substances may decompose,

[32] Erskine-Murray: Phil. Mag. (5), **45**, 403 (1898).
Kenrick: J. Phys. Chem., **16**, 515 (1912).
Bennett: Trans. Am. Electrochem. Soc., **23**, 394 (1913).
J. Phys. Chem., **17**, 373 (1913).

[33] Bennett: Trans. Am. Electrochem. Soc., **21**, 257 (1912).
J. Phys. Chem., **16**, 298 (1912).

[34] See Bennett and Brown: Trans. Am. Electrochem. Soc., **23**, 383 (1913).
Jour. Phys. Chem., **17**, 373 (1913).
See also Reichinstein: Zeit. Elektrochemie, **18**, 850 (1912).

being transformed into electricity, while the decomposition of the latter products cannot yield electricity, since they are in electrical contact with the electrode, and therefore short circuited. The excess energy required to form such products must therefore appear finally as heat.

With reference to the reducing power of the intermediate state of the metals, zinc for instance (Zn_1), it may be definitely said that it has a stronger reducing action than hydrogen liberated at the surface of a zinc electrode, for it has been shown that reductions can be performed during the deposition of zinc from sodium zincate,[35] which are not accomplished or are not carried out with such speed if a zinc cathode and sodium hydroxide as electrolyte be used. For instance, fifteen times more indigo white was formed from indigo blue when zinc was simultaneously precipitated than when hydrogen was liberated at a zinc cathode in sodium hydroxide. This cannot be due to the specific effect of the metal itself on the reaction, for zinc and acid do not reduce indigo blue. This can only mean that some substance is formed during the deposition of zinc which is a stronger reducing agent than massive zinc.

Several other cases of such intermediate action, showing unquestionably irreversibility, are also well known. The most common case[36] is the reduction of nitrates to ammonia. It is claimed by Shinn that it is best to have copper sulphate in the solution throughout the reduction at a copper cathode. The reduction to ammonia will go on, however, without the simultaneous deposition of copper.[37] With a nitrate solution, copper cathode and zinc anode, with a diaphragm, four Grove cells being used (probably 7-7.5 v.) the solution contained one part of ammonia to 20 parts of nitrate after four hours. The zinc-copper couple

[35] Binz: Zeit. Elektrochemie, **5**, 5, 103 (1898).
Binz and Hagenbach: *Ibid.*, **6**, 261 (1899).
Zeit. angew. Chem., **1899**, 489.
See also
Löb: Zeit. Elektrochemie, **2**, 532; **3**, 42 (1896); **4**, 428 (1898).
Haber: Zeit. phys. Chem., **32**, 258 (1900).

[36] Luckow: Zeit. anal. Chem., **19**, 11 (1880).
Easton: Jour. Am. Chem. Soc., **25**, 1042 (1903).
Shinn: *Ibid.*, **30**, 1378 (1908).
Smith: Electro-analysis, p. 292.
See also
Wohl: Ber., **27**, 1437, 1817 (1894), and
Tommasi: Monit. scientifique [4] **12**, 182 (1898).

[37] Gladstone and Tribe: Ber., **11**, 717, 722 (1878).

at 15° C. gives complete reduction after 24 hours. Smith's analytical method, with copper depositing, is complete after about one-half hour, using 4-5 amperes with a voltage of not over ten volts. It is certain therefore that copper simultaneously deposited, helps in the reduction. From what has been said above, it is evident that the intermediate products formed in the passage from dissolved ion to elementary material, as it is commonly known, are more active than either of the materials started with. In other words, in the case of hydrogen and the metals, the products are stronger reducing agents, while in the case of oxygen, chlorine, etc., the products are stronger oxidizing agents.

Let us now consider by how much the processes discussed above are irreversible. Langmuir[38] has calculated that the heat of formation of hydrogen molecules from active hydrogen is 90,000 calories. In passing from the dissolved ion to gaseous molecules if all of the ions went to H_1 which broke down generating heat only, and the reverse reaction generated no H_1 the reaction would be irreversible by 90,000 calories per 2 grams of hydrogen. This in terms of intensity would be

$$E = \frac{90{,}000 \times 4.18}{2 \times 96{,}500} = 1.9 \text{ volts.}$$

In other words, under these conditions of maximum irreversibility, electrical energy of 1.9 volts greater intensity would be required to form hydrogen gas molecules than that given by the reverse reaction. As a matter of fact, this maximum value could never be reached, for the reverse reaction requires necessarily a definite equilibrium of active hydrogen. This calculation serves to show that the intermediate product, which has been isolated, has an activity of sufficient magnitude to account for differences found experimentally.

Let us next inquire into the case of zinc. Suppose we take the first product of electrolysis Zn_1, as analogous to vapor. The molecular heat of vaporization of zinc from Trouton's law is $(950° + 275°)\ 20 = 24{,}460$ calories approximately, while the molecular heat of fusion is 1,840 calories, representing, as assumed above, irreversibility to the extent of 26,300 calories per gram molecule of zinc, or in terms of intensity

[38] Jour. Am. Chem. Soc., **37**, 457 (1915).

$$E = \frac{26{,}300 \times 4.18}{2 \times 96{,}500} = 0.56 \text{ volt.}$$

In other words, electrical energy of 0.56 volt would be used in depositing zinc, over that given by its solution, if during precipitation all of the metal went through the Zn_1 stage analogous to vapor, and during the reverse reaction none of the metal went through this stage. This maximum value could not be reached, however, for the same reason as given in the case of hydrogen.

There is one case where nearly the maximum value of hydrogen overvoltage may be obtained. In order to measure its value it is necessary to carry out the reaction $H_1^{\cdot} \rightarrow H_2$ in one stage without the possibility of conflicting reactions. If we take platinum or gold, place it in hydrogen gas and heat it to 300-400° C., it is found that the potential of the metal[39] is — 1.5 volts, as a maximum at 370°. That for oxygen under these conditions is + 0.8 volt, as a maximum. The maximum value is obtained when the gas pressure is lowered. The voltage generated is therefore due to the dissolved gas coming out of the metal into the gas phase.

When hydrogen or oxygen ionizes in a solution at the surface of platinum, for instance, the molecule dissociates, giving H_1 or O_1, which assumes a charge or charges becoming dissolved ion. The process goes on in two steps and equilibrium concentrations are maintained. The process is therefore not reversible, as has been pointed out above. When, however, hydrogen gas dissolves in gold, it is probably present as H_1; when this comes out into the gas phase, the reaction $H_1 \rightarrow H_2$ is carried on. This reaction is in one stage, and represents the energy which is lost in carrying out the electrochemical reaction, hydrogen ion to hydrogen gas. Thus it is probable that in this specific case where the intensity factor of the reaction $H_1 \rightarrow H_2$ is measured, we have a measure of the irreversibility of the process, $H^+ \rightarrow H_2$.

It is evident that there are intermediate products between dissolved ions and free gaseous molecules, or solid crystallized metals, the preparation of which requires more energy than is yielded by the opposite reaction. The activity of these substances is

[39] Hartley: Proc. Roy. Soc., **90**, A, 61 (1914).

wholly sufficient to account for the irreversibilities found experimentally in the case of hydrogen and zinc. It is only necessary to show how the plan may be formulated to explain overvoltage.

In the production or decomposition of one equivalent of zinc, one faraday of electricity is required or formed. The intensity or voltage is greater by about 0.10 volt for the precipitation than that given by the resolution of the zinc. This over or excess voltage is a measure of the irreversibility of the process. Hydrogen requires up to 0.75 volt more to precipitate than is yielded by the reverse reaction, depending on the metal at which it is deposited, and other conditions. Oxygen requires up to about 0.60 volt in excess of that given by the solution and ionization of the gas. This excess voltage is a direct result of an irreversible process, several cases of which have been discussed above. The mechanism of the reaction is just this. The voltage generated during solution is due to molecular material going to atomic material which ionizes. The atomic material is present only in equilibrium concentrations. In the reverse direction the voltage must be sufficient to build the concentration up beyond equilibrium else the reaction would not go on. The over or excess voltage will be low if the reaction

$$\text{atomic material} \rightarrow \text{molecular material}$$

is rapid, so that a low concentration of atomic material is had. If this reaction is slow the overvoltage will be high, for a high concentration of active material above equilibrium will be obtained. The overvoltage of gases will depend on the building up of concentrations above equilibrium of active or atomic material, while that of the metals will depend on atomic metal (M_1). The former will vary with the metal of the electrode and the nature of the solution, for these must have a catalytic influence on the reaction

$$\text{atom} \rightarrow \text{molecule.}$$

The overvoltage should be low where the metal shows strong catalytic action. This is actually found.[40] Overvoltage of metals, however, is simpler since it can exist only at its own surface, since the metal has to be deposited to exhibit this property and

[40] Lewis and Jackson: Zeit. phys. Chem., **56**, 193 (1906).
Berliner: Wied. Ann., **35**, 791 (1888).

have it measured. In fact since overvoltage is dependent on the reaction, ion to molecule, in any case, we should expect to find that when a stationary state is reached, the only factors which can vary overvoltage are factors which change this reaction. We know, for instance, that reactions are hastened by an increase in temperature. We should expect an increase in temperature to show a decrease of overvoltage. This has been noted many times and is seen in Table II,[41] which gives the overvoltage of hydrogen at a copper cathode. The current density was 1 milliampere per square centimeter.

TABLE II.

Temperature	Overvoltage
11.5°	0.33
20.0°	0.31
30.0°	0.28
45.0°	0.27
60.0°	0.25

Thus when the reaction is hastened by raising the temperature or when catalytic agents are present the overvoltage is low because the concentration of atomic material is kept low.

Conversely, it must be expected that any condition which tends to cause or allow the building up of concentrations of the active intermediate products above equilibrium, would raise the overvoltage by an amount depending on how much the concentration exceeds equilibrium values.

It is plain, too, that when conditions are right for low overvoltage, the reaction $2H_1 \rightarrow H_2$, for instance, takes place immediately, and therefore at the surface of the electrode, while as the overvoltage increases the sphere of the reaction moves further below the surface of the electrode. In other words, the conception of "electrode volume"[42] varying *directly* with overvoltage, is valid. This, however, has a more important bearing with reference to the ionization of the gas formed, which will be mentioned later.

Let us next consider some of the conditions which should give rise to higher concentrations of intermediate products and therefore higher overvoltage. An increase in current density, other conditions being the same, should increase the concentration of

[41] Pring and Curzon: *l. c.*
[42] Reichinstein: *l. c.*

active intermediate products. As a matter of fact the overvoltage increases with the current density, as the following table[43] shows:

TABLE III.

Current Density Milliamperes per Sq. Cm.	Hydrogen Overvoltage at			Oxygen Overvoltage at Platinum	Zinc Overvoltage at Zinc
	Lead	Platinum	Mercury		
10	0.62	0.06	0.54	0.56	0.089
20	0.64	0.06	0.45	0.56	0.089
40	0.71	...	...	...	....
50	0.70	0.06	0.40	0.56	0.090
100	0.67	0.07	0.30	0.56	0.091
200	0.66	0.08	0.07	0.56	0.092
300	0.64	0.08	0.08	0.55	0.094
500	...	0.05	0.04	0.55	0.094
1000	...	0.03	—0.01	0.55	0.095
2000	...	—0.03	—0.05	0.54	0.096

The overvoltage increases to a maximum with current density in the case of hydrogen at lead and platinum, and at higher currents decreases. It decreases at the surface of mercury, while oxygen overvoltage decreases slightly at high current densities. Zinc overvoltage increases steadily. If lower current densities had been used, hydrogen at mercury and oxygen at platinum would have shown maxima also. The decrease of overvoltage at high current density is to be explained in part by the rise in the temperature which we have seen lowers the overvoltage, but largely on account of the fact that the concentration of H_1 and O_1 becomes so great that they are forced to break down as soon as formed; namely, at the surface of the electrode. The highest current density used, it may be seen, is 200 amperes per square decimeter, which means that the electrode will all but be covered by a film of gas. In such concentrations it may be seen that the intermediate products would be so unstable that they would form molecular gas immediately. This is equivalent to saying that the ion goes directly to molecular gas, more or less reversibly. This would occur at the surface of the electrode. It is evident, therefore, that too great an increase of current density may tend to lower the concentration of active material by reason of hav-

[43] Newbery: *l. c.*

ing increased the speed of decomposition. In this case it is conceivable that the atoms lose their charge in close proximity to each other, and at the temperature used they combine at once, forming molecules. In fact Langmuir assumes that the formation and condensation of active gases takes place by the dissolved gas (in platinum or tungsten), which is in the atomic form, being driven out, traversing to the glass wall, which is cooled, without striking another atom. There is little doubt, therefore, that if these atoms come together they would react immediately. Furthermore, at the enormous current densities used, there is little doubt but that the atoms are formed in close enough proximity to come together. Thus the reaction of decomposition would be hastened and therefore the overvoltage lowered.

The case of overvoltage of zinc at a zinc electrode is different in that it steadfastly increased, although the increase is slight above 30 amperes per square decimeter. The reaction is different here, in that zinc atom goes to a polymerized complex consisting of half dozen or more atoms. It is evident that the polymerization of atoms to form a molecule of two atoms in the same state of aggregation may easily become instantaneous, but the polymerization to a molecule of half dozen or more atoms, going first to the complex representing the liquid, then the solid, and finally crystallizing, could not be instantaneous. Thus the effect is different with metals than with gases.

Besides the general effect that metals which show slight catalytic effect on the reaction causing irreversibility, show high overvoltage, the hardness of a specific metal may influence this phenomenon. A hard copper[44] electrode gives a higher overvoltage than one of soft copper. On the other hand, higher values are obtained with soft iron than hard iron. Electrolytically deposited copper gives maximum values while electrolytically deposited iron and nickel give minimum values. It should be noted that a low current density (0.1 ampere per square decimeter) was used. From the foregoing discussion the explanation is probably this. The electrolytic metal is hard, therefore we have to consider only the cases that hard copper and soft iron and nickel give maximum values of overvoltage. Nickel and iron are metals which take up hydrogen but do not readily catalyze the reaction

[44] Pring and Curzon: *l. c.*

$H_1 \rightarrow H_2$. Copper neither takes up hydrogen nor catalyzes the reaction. Soft iron and nickel would, therefore, take up more active hydrogen but the reaction of formation of molecules would not be faster than with hard metal. Thus the overvoltage would be increased by an amount depending on how much the concentration of active hydrogen is raised in the metal. In the case of copper, since practically no hydrogen is taken up, the change in the hardness does not affect the concentration of active hydrogen as in the other case. Hardening the metal serves only to confine the action to the surface and may be considered equivalent to an increase in current density.

The overvoltage probably always increases with time to a maximum and then remains constant or falls off slightly. The following values[45] illustrate this:

TABLE IV.

Overvoltage with Hydrogen at Platinum.

After Minutes	At Milliamperes per Square Centimeter	
	300	400
1	0.076	0.060
5	0.080	0.068
15	0.088	0.092
30	0.100	0.104
Hours		
1	0.112	0.120
6	0.173	0.236
12	0.471	0.200
24	0.511	0.120
5 min. off	0.08	....
10 min. on	0.122	....

These effects must be explained by assuming that the maximum concentration of active products, or saturation is not reached for a definite time. The addition of colloids tends to minimize time effects. The addition of colloids tends to raise the overvoltage of gases. This may be due to an increased adsorption of active gas, and a consequent increase in the stability.

Metal overvoltage is practically not affected by colloids, it

[45] Newbery: *l. c.*

being slightly raised in one case and lowered in another. From what has been said, this reaction is not affected by changes in conditions as much as the reactions in the formation of gases. This is particularly noticeable in that accurate and consistent results[46] are easily obtained here, while variation of 5 millivolts with hydrogen overvoltage at platinum and lead cathodes and of from 5 to 500 millivolts at mercury are encountered.

The effect of change of pressure on overvoltage has been studied,[47] and should be mentioned here. It was found that an increase of 100 atmospheres on the hydrogen gas pressure did not appreciably change the hydrogen overvoltage. This follows directly from the theory outlined above. There is practically no H_1, active hydrogen, in the gas above a solution and electrode during electrolysis. At least, we have found it impossible to obtain reduction of zinc oxide by placing it very close to the cathode during electrolysis. An increase of the gaseous hydrogen (H_2) pressure would not increase the pressure of H_1 as such. A change of pressure can only change the solubility of H_2 in the electrode. When, however, hydrogen dissolves in a metal, it is generally present in the atomic state, which means that when the concentration of H_2 in the electrode is increased there is an equivalent increase in the H_1 concentration. Any change of pressure, therefore, changing the concentration of H_2 tending to change the reaction $H_1 \rightarrow H_2$ must be accompanied by an equivalent change in the concentration of H_1 in the same direction tending to hold the reaction velocity constant. Therefore, very slight effects on overvoltage of gases should be noted by changing the gaseous pressure.

Another important property of gases newly formed by electrolysis is their ionization.[48] It has been shown that the charge carried by the gas may vary with the conditions, and also that the quantity of ionization[49] varies inversely with the overvoltage of the gas. For instance the metals arrange themselves in the order of decreasing ionization of hydrogen gas, thus

$$\text{Pt} - \text{Cu} - \text{Pb} - \text{Hg},$$

[46] Newbery: *l. c.*
[47] Newbery: *l. c.*
[48] Townsend: Proc. Camb. Phil. Soc., **5**, 9 (1897); Phil. Mag. (5), **45**, 125 (1898).
[49] Newbery: *l. c.*

which is the order of increasing overvoltage. In the case of hydrogen which has been studied, the ions[50] possible are H^-_1, H^+_1 and H^+_2. The latter ion is the ordinary gaseous ion, and is probably formed from gaseous hydrogen by the loss of an electron. At atmospheric pressures, the quantity of the ionized material relative to the un-ionized is very small indeed.[51] Furthermore, it is not difficult to ionize a gas. Ionization is caused by escaping steam,[52] when a cloud of dust is raised[53] and near waterfalls. Ionization may be produced by collisions[54] of other ions and under such conditions the voltage required for ionization of hydrogen is only about eight volts. It is beyond the scope of this paper to show the mechanism of the reaction of ionization of gases during electrolysis. One or two conclusions may be pointed out, however, which may throw some light on the subject. It has already been noted that as the overvoltage becomes low the sphere of the reaction moves to the surface of the electrode, that is, the reaction $H_1 \rightarrow H_2$ is instantaneous. Now since ionization means the setting free of charged particles of material, and since these charged particles exist as dissolved ions, that is, in the solution up to the metallic surface of the electrode, it necessarily follows that as the reaction of formation of gas approaches the surface, there exists greater possibility of contaminating the free H_2, for instance, with charged products. Thus the ionization should increase as the reaction approaches the surface of the electrode. In other words, the ionization should increase with decreasing overvoltage, as is actually found.

One suggestion as to the mechanism of the reaction might be made. If conflicting conditions are absent, only positively charged hydrogen is obtained at the cathode. In other words only under such conditions as the removal of positive hydrogen, is the gas charged negatively. How is the positively charged hydrogen freed if we neglect temperature and mechanical effects? At the surface the concentration of reacting material must be high. It is possible that the gas (H_2) carries mechanically with it a small

[50] Townsend: Phil. Mag. (6), **7**, 276 (1904); Proc. Roy. Soc., **80**, A, 207 (1908); **81**, A, 464 (1908).
See also Kleeman: Proc. Camb. Phil. Soc., **16**, Pt. 4, 286 (1911; Pt. 7, 621 (1912).
[51] Kleeman: *l. c.*, p. 286.
[52] Rudge: Proc. Camb. Phil. Soc., **18**, Pt. 3, 127 (1915).
[53] Rudge: Proc. Roy. Soc., **90**, A, 256 (1914).
[54] Pawlow: Proc. Roy. Soc., **90**, A, 405 (1914).

quantity of the ions in solution, just as in distillation liquids may carry small quantities of liquids or solids over even though the former be in the vapor state. The quantity need not be weighable, and the possibility of contamination is greater since these substances are probably in the same state of aggregation. In this way the gas might become charged positively by means of H^+_1, which is the same as the dissolved ion. The gas, however, is most often charged by means of H^+_2, since this is the ordinary gaseous ion. This may be obtained by the reaction of one atom of active hydrogen with one positive ion from the solution, thus

$$H_1 + H^+ \rightarrow H^+_2.$$

This reaction would increase as the sphere of the general reaction approached the surface bounding the heterogeneous system. It would therefore vary inversely with the overvoltage. From this viewpoint, therefore, it follows that ionization of the newly formed gases should vary inversely with the overvoltage of that gas.

From what has been said above, it may be concluded that:

1. Any chemical reaction, consisting of more than one step, in generating electricity cannot be strictly reversible, but requires more electrical energy to re-form the substances than is given by the reverse reaction.

2. This irreversibility gives rise to over or excess voltage, since the quantity factor is constant.

3. A general definition of overvoltage has been given.

4. A general and more elaborate theory of overvoltage has been developed.

5. This theory is that the excess of the back electromotive force of the system during electrolysis over the reversible electromotive force of the system consisting of the final products is due to the accumulation *during such electrolysis, of instable intermediate products above the equilibrium concentration.*

6. These products are unquestionably active hydrogen, H_1, active oxygen, O_1, etc., in case of gases, and M_1, atomic metal analogous to vaporized metal in the case of metal overvoltages.

7. These products have been shown to be more reactive than the final products and are sufficiently active to explain overvoltages found experimentally.

8. Active hydrogen has been shown capable of reducing cadmium from cadmium sulphate solutions, and reducing zinc from zinc oxide.

9. The theory put forward satisfactorily explains the known facts of overvoltage, a condition not satisfactorily met by previous theories.

Ithaca, N. Y.

DISCUSSION.

IRVING LANGMUIR: Haber pointed out in 1904 (Haber, Zeit. f. Electrochemie (1904) **10**, 433, 773) that we are not justified in accounting for the reactions and changes that take place with measurable velocity by means of assumptions involving concentrations as low as 10^{-10}. Haber considered particularly the potential of the silver electrode in solutions containing potassium cyanide. We all remember the Ostwald calculations, that there is only about one silver ion per liter in a silver solution to which potassium cyanide has been added.

Haber says that the potential of the silver electrode cannot possibly be determined by the presence of such small concentrations of ions, which in this case are as low as 10^{-24}. In fact, he concludes that any ion which is present in a concentration lower than 10^{-10} can have no appreciable effect on the electrode potential and I think that his arguments are absolutely unassailable.

I believe the authors here are making the same mistake in trying to account for overvoltage or any phenomena of that sort by means of such infinitesimal concentrations of atomic hydrogen in equilibrium, since these concentrations fall well below the limit of 10^{-10}, and therefore cannot truly determine the results.

This difficulty would be avoided if we knew more about the real mechanism of the phenomena involved in overvoltage. The condition of the surface depends, I believe, on the extent to

which the surface of the electrode is covered by adsorbed hydrogen atoms, and probably upon the degree of crowding of these in the surface layer. In some respects this "density of surface packing" may be equivalent to a concentration of atomic hydrogen, but in other respects there would be a vast difference between the two conceptions.

Since seeing the abstract of this paper, we have tried a few experiments on some of the questions raised by it, one in particular being whether atomic hydrogen can reduce zinc oxide. To determine this we put a series of oxides, made up into paste with water, on the inside of a bulb and had a tungsten filament in the center of the bulb, separated from the oxides by a loosely-fitting mica screen. Hydrogen was admitted in quantities in successive portions, and the tungsten filament was heated to a high temperature. We found that copper oxide is almost immediately and easily reduced to metallic copper by the atomic hydrogen which diffuses from the filament. Iron oxide is apparently reduced from ferric oxide to a lower oxide, but with zinc oxide we could not find any evidence of reduction. That does not mean there was not any at all, but there was no discoloration of the zinc oxide after several hours, whereas in the case of the copper oxide the metallic lustre of the copper appeared in a relatively short time, fifteen to twenty minutes. I doubt if zinc oxide can be reduced by atomic hydrogen at a reasonable rate.

C. W. Bennett: Did you use dry zinc oxide?

Irving Langmuir: Yes.

C. W. Bennett: We noticed this difficulty in some work done by Mr. O'Brien. When lithopone is exposed to ultra-violet light in the presence of hydrogen, the lithopone being dry and the hydrogen being dry, reduction does not take place at an appreciable rate. When, however, moisture is present, the reduction goes on very rapidly, with the blackening of the paste of lithopone. This same thing would occur in those cases where the zinc oxide is dry. We should expect no reduction in this case, but would expect to obtain the same results which were obtained by Dr. Langmuir in his experiment.

Irving Langmuir (*Communicated May 29*): More recent experiments, carried out over longer periods of time, have shown

distinctly that atomic hydrogen produced as above very gradually turns dry zinc oxide to a dark gray color, although silica (SiO_2) close beside it remains perfectly white.

W. R. Mott: On page 23 reference is made to ultra-violet light from flame carbons which I presume were the snow-white? I suggest that the so-called "blue" flame carbons are much richer in ultra-violet light.

A theory of the mechanism of overvoltage would help considerably if it would suggest a means of predicting the overvoltage position of metals. I suggested some generalizations along this line several years ago (Transactions Am. Electrochemical Soc. (1909) **15**, 569). The first point was that high overvoltage of hydrogen was given by metals of low melting point, such as mercury, gallium, tin, lead, zinc, etc., probably because of the great smoothness of their surface and the high surface tension of water. Conversely, metals of high melting points and presumably rougher surfaces, such as platinum, iron, cobalt, chromium, etc., have low overvoltages for hydrogen. The second generalization was that metals that absorb large volumes of hydrogen (10 or more) like platinum, chromium, palladium, nickel and cobalt tend to have low overvoltage, probably by facilitating the diffusion of the hydrogen through the metal. On the other hand, metals not known to form hydrides or depositing electrolytically with extremely small volumes of hydrogen, such as mercury of zinc, have high overvoltage. Such metals present a peculiar difficulty to the separation of hydrogen. Suppose we have a point of entrance of the hydrogen into the metal (whether as atomic hydrogen or a metal hydride might be debatable) then there must be some point at which the hydrogen can escape. If the metal is perfectly smooth, there would be the full surface tension of the solution to oppose the *initial* formation of a gas bubble. (The amount of energy per unit weight of gas is quite large for the initial formation of the gas bubbles.) On the other hand, if the metal were rough, then the surface tension of water opposing the *initial* formation of the bubble would be less. The movement of the hydrogen through the metal would be favored by the power of the metal to absorb hydrogen. The relation of resistance and overvoltage will come up later.

H. E. PATTEN: Dr. Langmuir quoted Haber's work to the effect that a concentration of ion in solution of 1×10^{-10} could not affect the equilibrium expressed by the potential of the electrode. Hydrogen at 1×10^{-7} is supposed to be in equilibrium with OH and to give the neutral point of water. That neutral point of water is reproducible, using the voltage from the hydrogen electrode. We also are able with fair reproducibility to get the hydrogen ion concentration using voltage measurement down beyond 1×10^{-10}, and that is not a trifling thing, it is being used at the present time as a measure for the rate at which certain bacteriological and physiological processes go on, and it is very important to know that we are not measuring the hydrogen ion concentration when we go down below 10^{-10}.

Personally I think other people working along this line would be indebted to Dr. Langmuir if he will give us an elucidation of what concentrations and what free acid we are measuring under those conditions.

IRVING LANGMUIR: I do not think that Haber's criticism applies to the measurement of equilibrium concentrations in solution. Haber does not say that these low concentrations do not actually exist in solution. He simply says that these quantities are too small to determine the observed potentials of electrodes.

H. E. PATTEN: The mass action law, it is true, does come into play if the hydroxyl ions are in large excess, and the hydrogen ions are in a minority, but we are basing our measurement on the hydrogen in equilibrium with that solution, and therefore the hydrogen determines as much as the hydroxyl what the voltage will be.

IRVING LANGMUIR: Haber argues that if the concentration of a given ion is less than 10^{-10}, the velocity with which the ions can possibly come in contact with the electrode is so small that it could not account for the current actually used in the measurement of the potential. He says that in the case of concentrations as low as 10^{-24} (which is the case with silver in potassium cyanide), the ions would have to move with a velocity greater than that of light in order to account for the observed phenomena. This is obviously impossible.

E. NEWBURY (*Communicated*): In this paper the authors have made a praiseworthy attempt to simplify the theory of overvoltage. Their conception of overvoltage as expressed on page 17 is identical with the modification of Le Blanc's definition given in my paper on the same subject (J. Chem. Soc. (1914) **105**, 2420). This idea of true overvoltage being the *excess back E. M. F.* is generally accepted by most of the present workers on the subject.

The main idea of the paper appears to be that overvoltage is entirely due to the presence of excess atomic hydrogen, oxygen, etc., which they believe to have higher solution pressures than the same bodies in the molecular state. In support of this, the authors mention many interesting cases of the vigorous action of active or nascent hydrogen.

This was proposed by me (*loc. cit.*), and is quoted by the authors. It is there suggested that excess or deficiency of intermediate metastable products, probably non-hydrated ions, is one of the causes of overvoltage. Of course, the non-hydrated ions lose their charges instantaneously and become atoms directly they touch the electrode, but whether the effect on the back E. M. F. is exerted before or after this discharge is to me still a doubtful matter. Probably some effect is produced in both states, but in any case the total effect can only be a small fraction of the total overvoltage, so may be deduced from a variety of considerations. Two examples will suffice to show this.

1. The overvoltage at the cathode when a metal is depositing is, in all cases so far observed, very low compared with that when a gas is being liberated. It therefore seems unreasonable at least to ascribe to all metallic atoms so much lower activity than to gaseous atoms.

2. Certain non-ionized organic compounds may be reduced by hydrogen at a platinum cathode with a current efficiency of 90 percent or more. Molecular hydrogen is quite incapable of such reductions, hence there must be at least 90 percent of atomic or nascent hydrogen present and yet the overvoltage is almost zero. Experiment shows further that in such cases the overvoltage of the electrode is *lowered* by the presence of reducible bodies, nitrobenzene for example, so that we are forced to the conclusion that

only a small fraction of the overvoltage can be produced by the presence of excess atomic hydrogen.

The observation of the effect of active hydrogen upon zinc oxide is very interesting. It might also be of interest if the authors were to try the effect of ultra-violet light upon the potential of a hydrogen electrode in a quartz tube.

It is unfortunate that the authors have readopted the idea of ascribing a catalytic action to the metals in hastening the reaction $2H = H_2$; more especially as they remark (p. 21) that the majority of the explanations already offered are unintelligible when it comes to a consideration of the exact mechanism of the reactions. To describe an action as "catalytic" is not an explanation, but merely placing it in a certain class which we do not fully understand at present, but hope to at some future date. Some catalytic actions have already been explained to some extent, *e. g.*, the action of iron or iodine as chlorine carriers, and to re-catalogue these as "catalytic" appears a retrograde step. In the present case also it is misleading. Graphite, gas carbon, palladium, etc., have great powers of absorbing hydrogen, so that their apparent overvoltages when first used as cathodes are negative. These cannot be accepted as true overvoltages, for the process is not a simple electrolysis. When these electrodes are saturated with gas and begin to liberate it in the form of bubbles, their overvoltages are anything but low. Palladium, for instance, takes its place among the high overvoltage metals, a position quite irreconcilable with the author's theory when the strong catalytic action of this metal is taken into account. The authors have apparently overlooked this fact (p. 31).

It appears that metal overvoltage is more satisfactorily explained by Le Blanc's theory, of which the second factor in my theory (*loc. cit.*) is only a slight modification.

There are many other points which might be mentioned which cannot easily be reconciled with the author's theory, but only one more need be given here. When platinum is used as cathode with a current density of 300 milliamperes per sq. cm., its overvoltage rises apparently without limit, being over 0.5 volt after 24 hours and still rising, in spite of the well-known catalytic power of platinum. If the surface of the metal is now examined microscopically, it appears unchanged from its original state. When

the current density is increased to four-thirds of its former value, the overvoltage again rises, but more rapidly than before, for 6 hours. It then begins to fall and after 24 hours has only half its maximum value and less than one-fourth of the maximum in the previous experiment. If now the surface of this metal is examined under the microscope, it is seen to be covered with tiny craters, suggesting most forcibly that the surface has been blown open by innumerable small internal explosions. I am quite unable to explain this set of experimental facts in any other way than by the idea that part, at least, of the overvoltage is caused by very great internal pressures of gas in the electrode, such gas being unable to escape except by solution or breaking the metal surface. Helmholtz has conclusively proved that increase of external pressure does alter the potential of a hydrogen electrode, a fact which has been overlooked by the authors, on page 36. My experiments on the effect of pressure merely showed that the potentials of the hydrogen electrode and of the experimental electrode were changed to approximately the same extent by change of external pressure within the limits stated, and that the *excess* potential or overvoltage was not appreciably affected. Hence the pressures in the electrode must be very great compared with 100 atmospheres.

The weak point in the theory suggested by me (parts of which are due to Nernst and Le Blanc) is the enormous pressures we must assume in explaining the very high overvoltages. While the internal pressures are undoubtedly very great, pressures such as 10^{20} atmospheres indicated by the theory pass the bounds of credibility. I have long felt this and hoped that Bennett and Thompson's ideas would help to explain matters, but more careful consideration showed that their theory is inadequate.

In the light of an extended research just completed, I hope shortly to publish my theory in an amended form, which will include not only overvoltage but also the closely allied phenomenon of passivity.

C. W. Bennett: Mr. Newbury loses sight of the fact that in going from ion to molecule we must pass through the atomic or nascent state. In other words all of the hydrogen must at some time be H_1. Overvoltage is conditioned only on the fact that the latter part of the reaction $2H_1 = H_2$, may or may not

be rapid. If it is rapid, a low overvoltage results. Suppose in this case there is present a relatively easily reducible substance at the cathode. Such H_1 as was present would be used up, and therefore it would be easy to form more. In other words the overvoltage would be lowered, as is actually found. I must insist on this: that *a relatively high absolute concentration of H_1 does not necessarily mean high overvoltage.* It is the concentration *above equilibrium* that counts.

It is claimed that palladium gives a high overvoltage, and that under similar conditions platinum also shows high overvoltage. After the electrolysis proceeds to a certain point, the electrode must be considered as a gas electrode and therefore different from that started with. When this is realized, the behavior is not phenomenal.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

OVER-VOLTAGE AND MONATOMIC HYDROGEN.

By Wilder D. Bancroft.

When an attack along any given line has failed for many years to yield any appreciable progress, it is always a good plan to see whether a radically different formulation of the problem may not help matters considerably. For more than fifteen years we have been trying to account for over-voltage on the assumption that the electrolytic decomposition of water is essentially a reversible one. This made it necessary to account for the abnormally large voltages observed at mercury cathodes and platinum anodes for instance. The total result is anything but gratifying from a theoretical standpoint. It is therefore desirable to see whether we can make more progress by starting with the assumption that the electrolytic decomposition of water is essentially an irreversible process, an intermediate product being obtained at the cathode which is a stronger reducing agent than hydrogen and which gives rise to hydrogen relatively slowly, while an intermediate product is obtained at the anode which is a stronger oxidizing agent than oxygen and which gives rise to oxygen relatively slowly.

We can make the requirements more definite. The intermediate cathode product must be a stronger reducing agent than cadmium, because cadmium can be precipitated electrolytically from a distinctly acid solution. The intermediate anode product must be a stronger oxidizing agent than ozone, hydrogen peroxide, persulphuric acid, or lead peroxide, because these substances may be formed electrolytically at the anode before oxygen is set free. The potentials of intermediate products having these properties are evidently sufficient to account for the over-voltages, and the problem is therefore to account for the values which we have hitherto called the normal ones. This is easily done, because the observed potentials will coincide with the values for the reversible evolution of hydrogen and oxygen, if specific electrodes catalyze

the reaction to such an extent that the concentrations of the intermediate products do not rise above equilibrium values.

This line of attack has been developed by Bennett.[1] The intermediate products are not necessarily compounds of the electrodes, because water is decomposed by radium emanation or by ultraviolet light,[2] the reaction products being hydrogen and hydrogen peroxide with varying amounts of oxygen, depending on the conditions of the experiment. Since hydrogen gas does not reduce oxygen gas to hydrogen peroxide, an active form of hydrogen must have been set free even though no electrodes were present. Any hydrides or oxides which may be formed during electrolysis with metal electrodes are therefore substances having lower potentials than the intermediate products, and these latter must be special modifications of hydrogen and of oxygen.

Bennett shows that Langmuir's electrically neutral monatomic hydrogen has all the properties which we need to ascribe at present to the intermediate cathode product, and he therefore concludes that this substance is electrically neutral monatomic hydrogen, while the corresponding anode product is probably electrically neutral monatomic oxygen. When the reaction $2H \rightarrow H_2$ takes place relatively slowly, we get high over-voltage. When the reaction takes place relatively quickly, we get low over-voltage. This point of view is not new; but it is timely. Ostwald[3] referred to it as a possible hypothesis and so did E. Müller.[4] It was brought forward seriously by Tafel[5] and was urged again by Lewis and Jackson[6] and by Brunner.[7] These men advanced the theory only to meet special cases and it seems not to have been accepted by anybody else. Bennett has emphasized the irreversibility and has generalized the application. The work of Langmuir gives an independent experimental confirmation which was lacking when Tafel and when Lewis and Jackson wrote.

The test of such a theory is its usefulness in accounting for other phenomena. The rapid breaking down of sodium amalgam when certain impurities such as iron, cobalt, or nickel are present[8]

[1] Trans. Am. Electrochem. Soc., **29**, 269 (1916).
[2] Soddy: The Chemistry of Radio-Elements, **14** (1915).
[3] Zeit. Elektrochemie, **6**, 40 (1889).
[4] Zeit. anorg. Chem., **26**, 11 (1901).
[5] Zeit. phys. Chem., **34**, 200 (1900); **50**, 641, 713 (1905).
[6] Proc. Am. Acad., **41**, 399; Zeit. phys. Chem., **56**, 207 (1906).
[7] Zeit. phys. Chem., **56**, 331 (1906).
[8] Walker and Paterson: Trans. Am. Electrochem. Soc., **3**, 185 (1903).

is due unquestionably to the decrease in the over-voltage, or, in other words, to the increased rate of formation of ordinary hydrogen from monatomic hydrogen.[9] It is for this reason that sodium amalgam must be made in porcelain vessels and not in iron pots or enamelled ware.[10] It is interesting to note that Aschan[11] attributes the slight reducing power of certain sodium amalgams to the fact that hydrogen is given off in the molecular form and is therefore inactive. It has taken us a long time to get back to the view that nascent hydrogen is monatomic hydrogen; but we are there at last. Bamberger[12] accounted for the enormous variations in the reducing power of different samples of zinc dust by saying that some give molecular and therefore inactive hydrogen. Nowadays we say that, owing to the increased catalysis of the reaction, $2H \rightarrow H_2$, the concentration of active hydrogen is less in certain cases than in others. The essential difference between the two points of view is that we know that the zinc dust was contaminated in one case by a metal having a lower over-voltage for hydrogen[13] so that we are not reducing at a zinc cathode, while Bamberger did not bother about the intermediate steps.

It is not solely the organic chemists who have to change their formulation. Peters[14] showed that platinum accelerated the evolution of hydrogen from a chromous chloride solution and Jablczynski[15] showed that mercury had no such action. It was considered that platinum catalyzed the reaction and that mercury did not. Today we say that hydrogen is set free at the platinum because of the low over-voltage for hydrogen and is not set free at the mercury because of the high over-voltage. The advantage of the latter point of view is that it shows the desirability of trying other metals with chromous chloride solution so as to find out at what degree of over-voltage the hydrogen ceases to be evolved rapidly.

It seems probable that an explanation can now be suggested for the remarkable results obtained by Fernekes[16] on the action

[9] *Cf.* Lewis and Jackson: Proc. Am. Acad., **41**, 403 (1906).
[10] Baeyer: Ber. deutsch. chem. Ges., **25**, 1255 (1892).
[11] Ber. deutsch. chem. Ges., **24**, 1865 (1891).
[12] *Ibid.*, **27**, 1548 (1894).
[13] Frederiksen: Jour. Phys. Chem., **19**, 696 (1915).
[14] Zeit. phys. Chem., **26**, 217 (1898).
[15] *Ibid.*, **64**, 750 (1908).
[16] Jour. Phys. Chem., **7**, 611 (1903).

of sodium amalgam on solutions. Fernekes found that alcohol and many other organic substances increased the rate of reaction between sodium amalgam and water. He accounts for the phenomenon by assuming the intermediate formation of hypothetical compounds between solvent and solute which are extremely instable towards sodium amalgam and therefore react very rapidly with it. While this explanation may be right, it has not proved helpful and is therefore useless, at any rate for the present. It seems probable that certain organic substances lower the over-voltage at mercury and consequently make the sodium amalgam instable. This hypothesis is susceptible of proof by direct experiment. While there are no measurements as yet made under conditions strictly comparable to those in Fernekes' experiments, Carrara[17] has shown that the over-voltages are quite different in methyl alcohol and in ethyl alcohol from what they are in water. I have often wondered whether the reason that nobody has ever prepared electrolytically a sodium alloy using a cathode of fused Wood's alloy, might not be because the over-voltage is not sufficient in this case.

While a high hydrogen over-voltage and high reducing power generally run parallel, it does not necessarily follow that all reductions will take place more readily at the cathode showing the higher over-voltage. Other factors may come in, as in the case of nitrates and nitrites. If the over-voltage were the only factor, it would not be possible for nitrates to be reduced more readily than nitrites at one cathode and less readily at another. This is the case, however.[18] At cathodes of zinc, iron, lead, platinum, and gold, nitrite is reduced more readily than nitrate. At cathodes of spongy copper or spongy silver, nitrate is the more readily reduced. Boehringer and Sons[19] claim that with hot solutions and a mercury cathode sodium nitrate is reduced much more readily than sodium nitrite. Caffeine is reduced more readily at a mercury cathode than at a lead one,[20] while the reverse is true with succinimide. Müller [21] has called attention to a number of

[17] Zeit. phys. Chem., **69**, 75 (1909).

[18] Müller: Zeit. anorg. Chem., **26**, 1 (1901); Zeit. Elektrochemie, **9**, 955 (1903); **11**, 509 (1905).

[19] Zeit. Elektrochemie, **12**, 745 (1906).

[20] Tafel and Neumann: Zeit. phys. Chem., **50**, 713 (1915).

[21] Zeit. Elektrochemie, **13**, 681 (1907); **14**, 429 (1908).

apparently abnormal cases and Chilesotti[22] has pointed out the peculiar behavior of molybdic acid at different cathodes. There are three distinct factors which may mask the relation between over-voltage and reducing (or oxidizing) power. One of the substances to be reduced may be adsorbed much more than the other, so that the effective concentration at the surface of the electrode may be very much higher than the mean concentration in the solution. The electrode may catalyze other reactions besides the one, $2H \rightarrow H_2$. This possibility was foreseen by Ostwald[23] a dozen years ago. A third possibility was pointed out to me by Mr. Bennett, that particular substances may catalyze the reaction, $2H \rightarrow H_2$, so that the over-voltage at a given cathode may vary with the nature of the apparently inert substances in the solution. We know that this happens when the solvent changes[24] to methyl alcohol or ethyl alcohol and we know that it happens when we add something which "poisons" the electrode.[25] In this paper it is not necessary to consider these points in detail. I merely wish to emphasize that the theory of over-voltage, as expounded by Bennett, does not require that high over-voltage and high reducing (or oxidizing) power necessarily go together, though this is usually the case.

In this paper it has been shown that the theory of the irreversible electrolytic decomposition of water gives us a very plausible explanation for some of the peculiarities of sodium amalgam, chromous chloride, and zinc dust. The normal relation between high over-voltage and high reducing power or oxidizing power may be obscured or made to disappear entirely in case of special adsorption of the reacting substance by the electrode, in case of a specific catalytic action of the electrode on the reaction, or in case of a catalytic action of the dissolved substance on the reaction, $2H \rightarrow H_2$, either directly or indirectly by affecting the electrode catalysis. The assumption of monatomic hydrogen as intermediate product at the cathode has proved useful as a working hypothesis. While we now consider nascent hydrogen as consisting in part of electrically neutral monatomic hydrogen, we

[22] *Ibid.*, **12**, 146, 173, 197 (1906).
[23] Trans. Am. Electrochem. Soc., **6** II, 187 (1904).
[24] Carrara: Zeit. phys. Chem., **69**, 75 (1909).
[25] *Cf.* Reichinstein: Zeit. Elektrochemie, **16**, 927 (1910).

recognize that the percentage of monatomic hydrogen may vary enormously and that nascent hydrogen from one source is not necessarily equivalent to nascent hydrogen from another source.

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DISCUSSION.

H. E. PATTEN: I would like to call attention to some phenomena to which Dr. Bancroft has only briefly alluded. I am quite sure that he has them in mind but he has not correlated them with this peculiar action of nitrates and nitrites and various electrodes. It has been pretty well shown in Edgar F. Smith's laboratory, namely by Easton and others, that if you have present in the solution being reduced some of the metal of the cathode salt, say copper sulphate, and let the copper deposit along with the hydrogen, then you get a larger percentage of your nitrate converted to ammonia. As was suggested, the catalytic effect of the spongy copper deposit has been used to account for this accelerating action.

This looks very reasonable, especially since the quantity of ammonia which you get is a function of the quantity of copper sulphate you have in solution. You may have too large a quantity of copper sulphate present, and then you do not produce enough hydrogen, and the reduction falls off, giving less ammonia.

To test out this same thing, some years ago I gave a paper before this Society on a series of experiments in which, in one case, the copper cathode was amalgamated with mercury in order to get a continuously smooth surface into which was then deposited the copper, in presence of KNO_3 and H_2SO_4. Now, as a check experiment, I had run the reduction of nitrate at a mercury cathode, and got a comparatively small amount of hydroxylamine. With copper sulphate present in solution you get nearly the same effect, with the accelerating effect of the freshly deposited copper.

I had expected that Dr. Bancroft and other people who are free to work as the spirit moves would have taken up that line

of work, especially as it has been shown to be true, also that cobalt and nickel and other salts of that nature behave in the same manner, the depositing of the metal on the cathode increasing the yield of ammonia from nitrate in acid solution.

Therefore, it would seem that the monatomic hydrogen idea would need to be considered in the light of the re-deposition of the cathode metal as it dissolves. If we put a cathode metal in acid solution it will be dissolved and plated back again. You will have an equilibrium effect and cannot help it.

W. D. Bancroft: Mr. Patten has assumed that because I am at a university I am a free agent and can work at anything I like. I cannot. I have got to get the students interested in their work, and for years I have been trying to get somebody to take up this problem of the action of nitric acid on different metals, to solve the question why you get nitrogen, nitrous oxide, nitric oxide, hydroxylamine and ammonia in the relative proportions obtained. Mr. Patten's ammonia problem is one special branch of that.

There is a perfectly wonderful field there, but for some unknown reason it does not appeal to any of the students. I present the subject to them every year and hope they will get interested in it, but they turn their back on it with great regularity. Perhaps some one else, therefore, had better look into it, but I can warn him in advance that he will have his hands full when he comes to the experimental side of it.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

DEPOLARIZATION BY ELECTRICAL WAVES.

By Wilder D. Bancroft.

Since we know now that hydrogen overvoltage is due to the concentration of electrically neutral monatomic hydrogen at the cathode rising above the equilibrium value,[1] it is possible to account for a phenomenon which appears to have puzzled people considerably, namely the effect of electrical waves on overvoltage. Bennewitz[2] electrolyzed sulphuric acid, using a very small platinum anode. When this anode was exposed to strong electrical waves, the potential against a hydrogen electrode was found to be 1.28, 1.27, 1.24 volts. Since the theoretical value for the hydrogen-oxygen gas cell is 1.23 volts, this means that the overvoltage at the oxygen electrode has been reduced to the negligible value of 0.01-0.05 volts. Bennewitz offered no explanation for the phenomenon and did not even discuss whether it was general or specific.

I think that we are safe in assuming that the phenomenon is general and not limited to this special case. It is therefore necessary to find a general explanation. From experiments on the disruptive discharge in gases, Schuster[3] concluded that there must be a layer of adsorbed gas on the electrodes having a high inductive capacity and therefore offering an increased resistance to the discharge. If this is true, it follows from the theorem of Le Chatelier that an electrical stress will tend to remove the film of adsorbed gas[4]. This conclusion can be used to account for the behavior of fountains, impinging jets, rolling drops, and soap bubbles, when electrified slightly. It is therefore a good working hypothesis. If an electrical stress tends to remove a

[1] Bennett: Trans. Am. Electrochem. Soc., **29**, 269 (1916).

[2] Zeit. phys. Chem., **72**, 223 (1910); *Cf.* Foerster: Elektrochemie wässeriger Lösungen, p. 293 (1915).

[3] Phil. Mag. [5] **29**, 197 (1890).

[4] *Cf.* Bancroft: Jour. Phys. Chem., **20**, 18 (1915).

gas from the surface of a solid, electrical waves will tend to remove active oxygen from the surface of an electrode and will therefore cut down the overvoltage, which is what Bennewitz found. We ought to find also that electrical waves cut down the hydrogen overvoltage. This has been shown to be the case by Rothmund,[5] whose paper seems to have been overlooked both by Bennewitz and by Foerster. More recently Archibald and von Wartenberg[6] have found that the anodic overvoltage is cut down when an alternating current is superposed on a direct current. Reitlinger[7] continued the work of von Wartenberg and sums up his results as follows: "Alternating current destroys the overvoltage due to direct current electrolysis, the potential difference between the electrode and the solution being decreased. The lower potential makes possible the isolation of intermediate products which are destroyed at higher potentials. When an alternating current is superposed on a direct current, there is an increase in the yield of the intermediate products and a decrease in the amount of the final products. Thus ozone is formed instead of persulphuric acid when sulphuric acid is electrolyzed. When alcohols are electrolyzed, aldehydes are formed instead of the corresponding acids. In an indirect way this confirms the experiments of Dony-Hénault, for he showed that aldehyde is formed from alcohol when the potential is kept sufficiently low, whereas acetic acid is the chief product when the potential is higher.

"It is only the negative portion of the alternating current which causes the lowering of the potential and makes possible the formation of intermediate products in relatively large amount. This is made clear in the experiments on ozone, for the potential falls and the yield of ozone increases only when the anode becomes cathode intermittently. With high-frequency currents the depolarizing action is less, owing to the great displacement of phase caused by the capacity of the electrodes."

About a year ago, Ghosh[8] published a paper on the effect of superposing an alternating current from an induction coil on a direct current. He found that the cathode effect is slight with

[5] Drude's Ann., **15**, 193 (1904).
[6] Zeit. Elektrochemie, **17**, 812 (1911).
[7] *Ibid.*, **20**, 261 (1914).
[8] Jour. Am. Chem. Soc., **37**, 733 (1915).

a platinum black cathode where the overvoltage is negligible, and is large with a mercury cathode where the overvoltage is high. He showed that the effect was due to the cutting down of the polarization; but he was unable to account for the phenomenon. "The alternating current acts primarily on the surfaces of the electrodes. Of course it is very difficult to suggest how it facilitates the liberation of the ions at the electrode surfaces, since we have not got very definite views as to the cause of the overvoltage phenomenon. It is not easy to imagine how an alternating current can destroy the supersaturation on the electrode surface, which is generally ascribed to be the cause of the overvoltage. The hypothesis that the alternating current somehow alters the nature of the electrode surface appears to be most reasonable."

As a matter of fact, the one assumption made by Schuster accounts for all these facts as well as for many others. An interesting corollary from the work of Rothmund, Bennewitz, Archibald and von Wartenberg, Reitlinger, and Ghosh is that with a sufficient depolarizing action at the anode lead peroxide should not be formed with lead electrodes in sulphuric acid because the formation of lead peroxide calls for an overvoltage of about half a volt.[9] This seems to have been confirmed experimentally by Ruer,[10] who used a very dilute sulphuric acid (2.5 percent) however and who seems to have obtained some lead peroxide at times. These experiments should be repeated with a more concentrated acid. With alternating current alone, lead sulphate is formed and no lead peroxide.[11]

Sufficiently strong electrical waves should also prevent the formation of sodium amalgam at a mercury cathode. Zinc, cadmium, and nickel should dissolve readily in sulphuric acid under similar conditions. Since lead peroxide is theoretically instable, there is a possibility of causing it to break down into lead oxide and oxygen. This seems not to have happened in Reitlinger's work for he used lead peroxide anodes in some experiments. Until we can make this reaction occur, it is hardly worth while to speculate on the fascinating possibility of making potassium chlorate break up at ordinary temperatures into potas-

[9] Dolezalek: Zeit. Elektrochemie, **5**, 537 (1899).
[10] Zeit. phys. Chem., **44**, 105 (1903).
[11] *Cf.* Schluederberg: Jour. Phys. Chem., **12**, 623 (1908).

sium chloride and oxygen, to say nothing of the more remote possibility of eliminating passive resistances to change in the case of organic compounds.

The experiments of Margules[12] and of Ruer[13] on the dissolving of platinum find their explanation in the cutting down of the overvoltage, as was recognized explicitly by Reitlinger.[14] With a direct current we get oxidation to a higher and insoluble stage. With alternating current the overvoltage is decreased and we get little or none of the insoluble compound.

There is one other point of distinct interest with respect to electric waves. The more recent determinations of overvoltage have given lower values than those obtained by Caspari.[15] This may be due to experimental error on Caspari's part. On the other hand, many of the recent determinations have been made with an intermittent direct current, the polarized electrode being connected with the potentiometer circuit during the breaks. It is possible that the polarization might have been cut down somewhat by induced currents during the make and break. If this were so, the measurements by this method would be in error. It may be that the error from this source is negligible; but this should be proved and not assumed.

The general results of this paper are that electrical waves must cause depolarization if we admit that electrical stress cuts down the adsorption of a gas by a solid. This assumption is a necessary consequence of Schuster's work on disruptive discharges and has been shown to account for the behavior of fountains, impinging jets, rolling drops, and soap bubbles, when electrified slightly. It is shown that electrical waves do decrease overvoltage at the cathode and at the anode, and that the assumption accounts for all the facts so far known. It is also pointed out that measurements of decomposition voltage involving the use of an intermittent direct current are subject to an error which is perhaps not negligible.

[12] Wied Ann., **65**, 629; **66**, 540 (1898).

[13] Zeit. phys. Chem., **44**, 81; Zeit. Elektrochemie, **9**, 235 (1903); **11**, 10, 661 (1905); Haber: Zeit. anorg. Chem., **51**, 365 (1906).

[14] Zeit. Elektrochemie, **20**, 261 (1914).

[15] *Cf.* Bennett: Trans. Am. Electrochem. Soc., **29**, 269 (1916).

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DISCUSSION.

H. E. PATTEN: There is one point Dr. Bancroft has not brought up, and that is the relationship between the electromotive force and the current in an alternating circuit. It was shown a good many years ago by Le Blanc, in his work on Alternating Current Work in Electrolysis, and by Dr. Crew at the Northwestern University, and Baker in a paper on the history of the arc spectrum (which apparently would not have any relation to this subject) that the lines of the spectrum which come out at various times after starting the arc depend on the relation of capacity and inductance in the circuit—in other words, whether the electromotive force is in step with the current. The value of the power factor, or the percentage of alternating-current energy available to do the work, is important. You may superpose an alternating current upon a direct current, especially when you are polarizing products at the electrodes, but you are bound to put the electromotive force out of step with the current, and get different products through being out of step.

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POLARIZATION IN LE CLANCHÉ CELLS.

By Duncan A. MacInnes.

In a recent number of these Transactions[1] Thompson and Crocker have presented a discussion of the cause of polarization in LeClanché primary cells which may be summarized as follows: Polarization will, in general, result when there is an accumulation of the products, or an insufficient supply of the factors, of the reactions taking place in a cell. The reactions of the LeClanché cell may be written in the two steps:

$$Zn + 2NH_4Cl = Zn\ Cl_2 + H_2 + 2NH_3 \qquad (1)$$

$$H_2 + 2Mn\ O_2 = Mn_2O_3 + H_2O \qquad (2)$$

Since the concentrations, or rather the activities, of the solid substances may be considered as constant, the polarization may be caused by an accumulation of H_2, $ZnCl_2$, or NH_3, or an insufficient quantity of NH_4Cl. As ammonium chloride and zinc chloride are present in excess in the electrolyte, the polarization must be due either to hydrogen or to ammonia. Thompson and Crocker's experiments, described in the paper mentioned, show that no hydrogen gas is evolved from the cell while in action, and that the pyrolusite combines quantitatively with it as it is formed. They conclude that hydrogen can not be the cause of the polarization. The one remaining substance is ammonia. To show that this can cause a lowering of the voltage of the cell if allowed to accumulate, the authors give measurements of the electromotive force of cells of the type

$$Hg \mid Hg\ Cl, KCl \mid NH_4Cl, NH_4OH \mid MnO_2, C$$

Increasing the NH_3 concentration around the carbon-manganese dioxide electrode from zero to five percent produced a decrease

[1] Trans. Am. Electrochem. Soc., **27**, 155 (1914).

of the potential of the above cell of 0.26 volt, if the ammonium chloride was dilute. The same change of ammonia concentration lowered the voltage only 0.09 volt if the ammonium chloride was saturated, as it is in the practical cell.

It appears to the writer that the formation of free ammonia is insufficient to account for polarizations of the order of half a volt or more, since the ammonia concentrations can hardly exceed five percent, even momentarily. The paper referred to gives many measurements of polarizations of over 0.5 volt. The fact that hydrogen is not evolved at the cathode of the LeClanché cell does not prove that it is not largely responsible for the polarization observed. The gas will be evolved only when its pressure on the electrode reaches one atmosphere. The action of the manganese dioxide is to keep its pressure far below this. Regarded separately, the system: MnO_2 — Mn_2O_3 — H_2 — H_2O, is univariant, since it has three components and four phases. Under equilibrium conditions the system will have a definite, though very small, hydrogen pressure for each temperature. If allowed to stand on open circuit the positive electrode of the LeClanché cell will reach a voltage corresponding to the solution tension of hydrogen at this equilibrium pressure.

A calculation of the value of this equilibrium pressure may be of interest. The electromotive force of the cell can be considered as the sum of the voltages of the two parts of the double cell:

$$\text{Zn} \left| \begin{matrix} NH_4Cl \\ ZnCl_2 \end{matrix} \right| \begin{matrix} H_2 \\ 1 \text{ atm.} \end{matrix} \quad — \quad \begin{matrix} H_2 \\ 1 \text{ atm.} \end{matrix} \left| \begin{matrix} NH_4Cl \\ ZnCl_2 \end{matrix} \right| \begin{matrix} H_2 \\ x \text{ atm.} \end{matrix} \qquad \text{(A)}$$

As will be observed, the potentials of two added hydrogen electrodes will cancel each other. The electromotive force of the cell

$$\text{Zn} \left| \begin{matrix} 15\% \ NH_4Cl \\ 5\% \ ZnCl_2 \end{matrix} \right| \begin{matrix} H_2 \\ 1 \text{ atm.} \end{matrix}$$

has been determined at 25° by the writer, and found to be — 0.514 volt. In this measurement the negative electrode consisted of an amalgamated rod of pure zinc. The hydrogen electrode, which was of the form described by Hildebrand[2] consisted

[2] J. Am. Chem. Soc., 35, 847.

of a platinized-platinum electrode over which hydrogen gas was passed at one atmosphere pressure. The voltage of the cell:

$$\begin{matrix} H_2 \\ 1 \text{ atm.} \end{matrix} \Big| \text{ electrolyte } \Big| \begin{matrix} H_2 \\ x \text{ atm.} \end{matrix}$$

is independent of the nature of the electrolyte and may be calculated by means of the equation[3]

$$E = \frac{RT}{2F} \ln \frac{P}{1}$$

This equation can be obtained by integrating the purely thermodynamic equation

$$- V \, dp = 2 F \, dE$$

using the perfect gas law $P\ V = R\ T$ as the equation of state of hydrogen. (E = electromotive force, R = the gas constant, T = absolute temperature, F = the faraday, and P = the pressure of hydrogen.) Assuming that the electromotive force of the LeClanché cell on open circuit has the average value of — 1.50, the voltage of the right-hand part of cell A will be

$$- 1.50 - (- 0.514) = - 0.986.$$

Substituting this value in equation 3 and using $R = 8.31$, and $F = 96{,}500$, we obtain $P = 4 \times 10^{-34}$ atmospheres for the pressure of hydrogen on the cathode of a LeClanché cell at equilibrium.

Upon taking current from a cell it is probable that the reaction represented by equation 1 will proceed more rapidly than that of equation 2, and that the hydrogen pressure will rise above the equilibrium value. A calculation similar to the above will show that for a polarization resulting in a drop of voltage of a cell to — 1.20 will result from a rise of the hydrogen pressure from 4×10^{-34} to 6×10^{-24} atmospheres. These figures are, of course, approximate, since some polarization must be due to changes in the electrolyte resulting from the passage of the current. Thompson and Crocker's figures show, however, that such changes are small. With $Zn\ Cl_2$ in the electrolyte polarizations from this source must be still smaller than that indicated in their experi-

[3] Le Blanc, *Electro-Chemistry*, page 195.

ments, since $Zn\ Cl_2$, as is well known, will form compounds with ammonia.

There is also the possibility, suggested by Allmand[4], that the current is carried from the electrolyte not by the discharge of hydrogen ions, but by the direct change of valence of the manganese compounds, as represented by the reaction:

$$2Mn^{++++} \pm 3OH^{-} = Mn_2O_3 + 3H_2O + \oplus \qquad (3)$$

Whether reaction 3 or reaction 1 takes place depends on the relative velocities of these reactions. The equilibrium pressures of hydrogen are the same in either case.

DISCUSSION.

N. K. Chaney (*Communicated*): Dr. MacInnes is evidently under the impression that Thompson and Crocker have successfully eliminated from consideration all but two factors in the polarization of LeClanché cells; namely, the accumulation of free hydrogen and free ammonia at the manganese dioxide electrode; and further, that to prove the absence of one of these factors is to force the acceptance of its alternative.

With this understanding MacInnes proceeds to impale Messrs. Thompson and Crocker upon the hydrogen horn of their own dilemma, by pointing out that the ammonia polarization is utterly insufficient to account for the observed results. From this it follows either that the hydrogen pressures calculated by MacInnes have a real existence, or else that the supposed alternative is imaginary.

As a matter of fact Thompson and Crocker have not been so unguarded in their statements as MacInnes supposes, and have provided for themselves a way of escape from the latter's conclusions, as well as from their own.

While they state in so many words that "The cause of polarization in the LeClanché cell must therefore be the other cathode

[4] "Applied Electrochemistry," page 206.

product, the ammonia" this is qualified further on by the statement that "the removal of the ammonia . . . should prevent polarization, *except in so far as it is the result of the using up of the pyrolusite.*" In other words the reasonable suggestion is offered that the chemical changes occurring in the manganese dioxide may need consideration as a possible factor in its electrode potential, quite irrespective of possible polarization by hydrogen or ammonia. I shall show that this obvious but strangely neglected consideration is quite sufficient to account for any polarization phenomena which stands in need of explanation.

MacInnes is correct in saying that Thompson and Crocker's failure to observe the evolution of free hydrogen from a manganese electrode is no proof of the absence of hydrogen at lower pressures. But his paper proves the possibility—not the existence—of such hydrogen pressures upon the manganese electrode.

Reactions (1) and (2) as stated in his paper, *i. e.*,

$$Zn + 2NH_4Cl = Zn\,Cl_2 + H_2 + 2NH_3 \qquad (1)$$

$$H_2 + 2MnO_2 = Mn_2O_3 + H_2O \qquad (2)$$

beg the question by assuming the existence of a free molecular hydrogen phase, which is exactly the point at issue. He writes the reaction as proceeding in two stages, in the first stage free molecular hydrogen is formed, in the second stage the molecular hydrogen reacts with the manganese dioxide. The validity of his subsequent application of the phase rule to these reactions depends upon whether the intermediate hydrogen phase as written has any existence in fact.

His reactions further involve the assumption that there are but two solid phases, MnO_2 and Mn_2O_3. Our own investigations have shown us that the reduction of MnO_2 may proceed to the Mn_3O_4 oxide and even to MnO.

Therefore, we have the possibility of an additional solid phase which would make the system non-variant instead of univariant as stated by MacInnes. Further complications are afforded by the possibility of solid solutions between these various manganese oxides.

In brief, equations (1) and (2) arbitrarily introduce a hydro-

gen phase the existence of which is in question, and assume the absence of solid phases of the manganese oxides which are very possibly present. This is hardly safe ground for the use of the phase rule as *a priori* evidence of the existence of a definite hydrogen equilibrium pressure on manganese dioxide electrodes.

A further consideration will show that even if the assumptions as to the above equilibria were justified, the velocity of their attainment at ordinary temperatures must be exceedingly slow and hence would be of no practical significance in explaining reactions which proceed with the velocity of depolarization phenomena. Manganese dioxide does *not* react with molecular hydrogen with appreciable rapidity at ordinary temperature. Nor apparently do Mn_2O_3 and H_2O spontaneously react to form MnO_2 and H_2, as the diffusibility of the hydrogen phase would require if reaction (2) was really reversible.

It may be concluded that the existence of a free hydrogen phase upon the manganese dioxide electrode cannot be settled by *a priori* reasoning and resort must be had to more direct experimental evidence.

If a cell be made up as suggested by Thompson and Crocker, consisting of a solid block pyrolusite as cathode, a zinc anode and the usual electrolyte, and if this cell is placed in continuous service, it will be found that the working voltage will increase rather than decrease for a time. When the voltage does begin to fall it is found that permanent changes have occurred in the exposed surface of the manganese electrode which has definitely lowered its working potential. These chemical changes are of sufficient magnitude to account for any observed polarization phenomena, the other factors are doubtless present to some extent. However, there is no necessity for believing that the observed polarization of manganese electrodes is due to free hydrogen although it is not unrational so to do. There are on the contrary some reasons to doubt it.

Among these is the fact that there is no observable polarization upon the initial circuiting of a standard dry cell. The observed drop in working voltage is wholly accounted for by the inter-resistance of the cell.

This does not coincide with the idea that the primary cause of polarization is the slow reaction velocity between hydrogen

ions and manganese dioxide, which thus caused a piling up of molecular hydrogen to be consumed by the manganese at its leisure.

D. A. MacInnes (*Communicated*): In my paper I avoided saying that the polarization of the Le Clanché cell is necessarily produced by gaseous hydrogen, and the possibility of other reactions is suggested. The main purport of the calculations is to show that hydrogen evolution can not be expected to take place until the voltage of the cell has dropped to about half a volt. What the actual mechanism of the polarization is depends on the relative velocities of the possible reactions taking place about an electrode, and can only be determined by experiment. The equilibrium pressures and concentrations will be independent of these velocities, and will depend only on the voltage of the cell. If polarization proceeds far enough to produce a chemical modification of the depolarizing substance the hydrogen pressure will adapt itself to the new conditions, provided the speed of the necessary reactions is great enough. The observations in the preceding criticism are of interest and value, but it does not seem to me to be necessarily true that hydrogen will not under any conditions react with manganese dioxide at room temperature. Also considering the order of magnitude of the pressures involved, how is it possible to prove the absence of hydrogen in equlibrium with MnO_2, Mn_2O_3, and H_2O? It is unnecessary to point out that if pressures are small diffusion phenomena will be of the same order. And how is the rise of the voltage of a polarized cell on standing on open circuit explained if the polarization is altogether due to a chemical modification of the depolarizer?

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

ELECTROLYTIC FORMATION OF PERCHLORATE.

By C. W. Bennett and E. L. Mack.

The usual conception of the mechanism involved in the anodic formation of perchlorates from chlorates is largely due to Oechsli[1] and his theory has gradually found its way into the text-books of electrochemistry with the result that it is at the present time commonly accepted as representing the actual mechanism of the process.

According to this theory the reaction at the anode during chlorate electrolysis is not to be considered a direct addition of oxygen to ClO_3 with the formation of ClO_4 but rather as a more complicated process, during which we must suppose the liberation of the chlorate ion. The various steps involved are, briefly, as follows: Chlorate ion is liberated by the current and, assuming that it acts in a manner analogous to other strongly acid anions, reacts with water at the anode with the formation of free chloric acid and liberation of oxygen,

$$2ClO_3 + H_2O = 2HClO_3 + O. \qquad (1)$$

The free chloric acid generated in this way is probably at a very high concentration in the film of electrolyte which is in immediate contact with the anode. Since in this condition it is known to be very unstable, spontaneous decomposition takes place, perchloric and chlorous acids being formed,

$$2HClO_3 = HClO_4 + HClO_2. \qquad (2)$$

The free chlorous acid thus formed very evidently cannot remain in the solution as such, since in contact with the chloric acid present it would immediately evolve chlorine dioxide:

$$HClO_3 + HClO_2 = H_2O + ClO_2. \qquad (3)$$

[1] Zeit. für Elektrochem., 9, 807 (1903).

This evolution of chlorine dioxide has never been observed to take place during this process, and the theory, therefore, assumes that the chlorous acid formed as shown in (2) is immediately oxidized to chloric acid by the oxygen from the decomposition of water by the liberated ClO_3 ions, as shown in equation (1).

The sum total of the reactions which, according to this theory, takes place at the anode may then be represented by:

$$2ClO_3 + H_2O + 2(F) = HClO_4 + HClO_3.$$

Oechsli, in order to satisfactorily explain the formation of perchlorate, finds it necessary to assume the liberation of the chlorate ion mainly for the following reasons. Oxygen, when discharged under conditions such that the electrode is reversible, probably requires a lower voltage than that needed for the liberation of oxy-acid anions;[2] but if we deal with an electrode which is not reversible toward oxygen, that is, where the discharge of oxygen requires a considerable overvoltage, a point may be reached at which the discharge of the oxy-acid anion will become easier, or require a lower voltage, than that for oxygen and will consequently take place. From this standpoint, assuming that ClO_3 is discharged, the formation of perchlorate could be expected to take place only at an anode where the overvoltage for oxygen liberation is sufficient to allow the preferential discharge of the chlorate ion. It is held that this hypothesis is supported by the following facts: (1) Perchlorate formation goes on with a markedly higher efficiency at a smooth platinum anode, where oxygen overvoltage is known to be high, than at an anode of platinized platinum, where oxygen discharge takes place much more easily. (2) If the solution is made alkaline at the anode the efficiency of perchlorate production falls off rapidly; a fact which is explained by the increased ease of oxygen discharge in a solution containing a high concentration of hydroxyl ions. The result is a discharge of oxygen along with the chlorate ions and a consequent drop in the anode efficiency. (3) This hypothesis best explains the rise from a comparatively low efficiency at the beginning of the electrolysis to a higher value as the electrolysis proceeds. When the oxidation is taking place at a high efficiency

[2] Bose: Zeit. für Elektrochem., 5, 169 (1898).

and the current is interrupted for a short time, it is found, upon closing the circuit, that the efficiency is low just as it was during the first few minutes of the experiment. The idea is that during the break in the current flow the concentration of free chloric acid at the anode falls, largely through diffusion, and that a certain length of time is necessary for the chloric acid to accumulate to that concentration in which it is unstable. During this time oxygen is evolved and the current efficiency necessarily falls. (4) Changing from a smooth platinum anode to one of platinized platinum brings about a marked decrease in efficiency and this is best explained by considering it equivalent to a decrease in current density because of the larger surface presented by the platinized electrode. At this lower current density the efficiency must be lower because we would have more oxygen librated in proportion to the number of chlorate ions than at the higher current density. Furthermore, many other electrochemical reactions which are commonly considered as being due to anion liberation show this same characteristic of decreased efficiency with platinized anodes. The formation of persulphuric acid and Kolbe's[3] synthesis of ethane are cited as being processes of this type. (5) An increase of temperature, at a fixed current density, brings about a decrease in perchlorate formation and a corresponding increase in oxygen discharge. This is considered to be the result of increase in hydroxyl ion concentration caused by the increased dissociation of water at the higher temperature. (6) Finally, perchlorate formation must be conditioned by chlorate ion discharge since the reaction has not been duplicated chemically; that is, chlorate has not been oxidized to perchlorate by chemical oxidizing agents.

This theory is open to the objection that it rests upon several assumptions which may or may not be true. We have no direct evidence that chloric acid, when sufficiently concentrated, decomposes with the formation of perchloric and chlorous acids. The visible products of the decomposition are known to be perchloric acid, chlorine dioxide, chlorine and oxygen. While the intermediate formation of chlorous acid is possible it has not, up to this time, been demonstrated satisfactorily. If we are to reason from analogy to the reaction which takes place when alkali chlo-

[3] Liebig's Ann., 69, 257 (1849).

rates are heated[4] it would appear much more probable that the primary decomposition products would be perchloric and hydrochloric acids.

Granting, however, that the liberated chlorate ion and free chloric acids would act in the manner assumed, the theory is still unsatisfactory in that it does not explain the decrease in yield of perchlorate on substitution of platinized for smooth platinum anodes or the marked fall in efficiency with rising temperature. In the former case, using a platinum anode a current efficiency of 97.0 percent was noted,[5] while with a platinized anode, the other conditions remaining unchanged, the efficiency dropped to 2.7 percent. It is very evident that it would be necessary to assume a tremendous decrease in current density to account for the marked efficiency drop at the platinized anode since a succeeding experiment shows that, under like conditions, using a smooth platinum anode and a current density approximately one-fourth that in the first experiment cited, the efficiency fell only to 92.0 percent.

Regarding the temperature effect it may be stated with certainty that the increase in the dissociation of water with a temperature rise of 73° is insufficient to account for a decrease in efficiency of 97 percent. The efficiency at 7° is 97 percent, while no perchlorate is formed at 80° C., other conditions remaining unchanged.

It has seemed advisable, therefore, to postulate that the electrolytic formation of perchlorate does not depend upon the liberation of the chlorate ion but rather is to be considered as a direct addition of oxygen to the chlorate ion. The object of this paper is to show that the phenomena observed during perchlorate formation are most easily and satisfactorily accounted for from this viewpoint. It is further proposed to furnish independent proof that chlorate may be oxidized to perchlorate by strictly chemical means; that is, under conditions where the liberation of chlorate ion cannot be assumed.

Let us consider for a moment the conditions existing at an insoluble anode during electrolysis of solutions containing oxygen or hydroxyl ions. Recent investigations[6] have shown that the

[4] *Cf.* Scobai: Zeit. phys. Chem., **44**, 319 (1903).
[5] Oechsli: *loc. cit.*, pp. 812 and 818.
[6] Bennett and Thompson: Trans. Am. Electrochem. Soc., **29**, 269 (1916).

action of the electrolyzing current is to liberate oxygen in the active or atomic form. This oxygen unless depolarized by some substance present at the anode will be converted into molecular or gaseous oxygen, the reaction represented by:

$$2O_1 = O_2$$

Further, it has been pointed out that the rate of this reaction, and consequently the concentration of active oxygen, or O_1, which is present at the anode at any given time, is dependent upon (1) the nature of the anode material, (2) the current density, (3) temperature, (4) nature of the solution, and (5) the elapsed time of electrolysis.

Schoch[7] has pointed out that only an *exceedingly small* voltage is required to discharge oxygen or any other ion into an electrode which is absolutely free from electromotively active material, and it follows from this and the above statement that the potential of the anode, at any given time, in a solution capable of discharging oxygen, depends primarily upon the concentration of active oxygen then existent at the electrode. Thus we see that by properly varying the conditions we may have oxygen discharged at any potential above a certain minimum value which is determined by the equilibrium value of the equation

$$2O_1 \leftrightarrows O_2$$

at the particular anode and under the particular conditions in question.

It may be well to point out here that in order to oxidize a given substance present in the electrolyte, chlorate for instance, it is necessary that the potential of the anode should rise *not to that point necessary to bring about the liberation of gaseous oxygen,* as is commonly believed, *but only to that point necessary to produce a concentration of active oxygen sufficient to oxidize the chlorate ion.* That this is the case and that the potential necessary for the latter process is very much less than that required for the former is conclusively shown by the work of Schoch.[8] Using a N/3 potassium chlorate solution and an iron anode it was found that the formation of perchlorate began when the anode potential

[7] Jour. Phys. Chem., **14**, 665 (1910).
[8] Jour. Phys. Chem., **14**, 735 (1910).

reached + 0.023 volts,[9] while a succeeding experiment showed that at an iron anode oxygen is not evolved until an anode potential of + 1.5 volts is reached.

This experiment, even without the support of further evidence, shows that the formation of perchlorate is not determined by the liberation of chlorate ion since no one would claim for this ion a discharge potential as low as + 0.023 volts. Most of the attempts at measurement have obtained values around + 1.37 volts.[10]

Having thus shown that perchlorate can be produced at an anode potential far below that required for the liberation of oxygen as well as much below that commonly assigned for ClO_3 discharge, let us consider the phenomena actually observed during the electrolysis of a chlorate solution, assuming the formation of perchlorate to be the result of a direct addition of oxygen to the chlorate ion.

Using a smooth platinum anode in a strong neutral chlorate solution with a current density of, say 4 to 6 amperes per square decimeter, we find the efficiency of perchlorate formation to be high, possibly as high as 95 percent. The anode potential is also found to be high and from the standpoint taken we consider that we now have at the anode active oxygen in such concentration that it is able to oxidize the chlorate ion rapidly and with good efficiency. We know that we are here dealing with an anode which exhibits a high overvoltage. This means that the concentration of active oxygen is above the equilibrium value. If we decrease the current density below the value first taken, we find a decrease in current efficiency with respect to perchlorate formation and a corresponding decrease in anode potential. This becomes intelligible when we consider that at moderate current densities oxygen overvoltage, and consequently concentration of active oxygen, decreases[11] with decrease of current density. Again, if the temperature be raised, we find the current efficiency decreases markedly. This, again, is in accord with the view taken since we have seen that the concentration of active oxygen pres-

[9] All potentials given in this paper are the observed readings against the normal calomel electrode. The signs are those observed in the experimental arrangement. This is in accord with the suggestion of Luther. See Le Blanc: Textbook of Electrochemistry, 4th Ed., 245.

[10] Le Blanc: Zeit. phys. Chem., 8, 299 (1891).

[11] Bennett and Thompson: *loc. cit.*

ent at the anode at any given time is dependent upon the state of the equilibrium

$$\text{active oxygen} \leftrightharpoons \text{oxygen molecule.}$$

Increased temperature tends to shift this equilibrium in favor of molecular oxygen and we would expect, therefore, a lower active oxygen concentration and consequently a lower oxidizing power. A sufficiently high current density at the higher temperature would, however, tend to increase the rate of production of active oxygen and increase its concentration in the electrode. As the current density is increased, we should therefore expect to obtain a consequent rise in efficiency of chlorate oxidation tending to overcome the inhibitory effect of the high temperature. This is actually realized experimentally.[12] The current density used was 16 amperes per square decimeter and with the solution maintained at 80° gave a current efficiency of 13.5-14.8 percent. This was raised to 40.0-42.5 percent when the current density was increased to 20.8 amperes per square decimeter, the temperature remaining constant at 80°.

If the solution is made alkaline the current efficiency falls off rapidly, a fact which is explained without difficulty when we recall that the discharge potential for oxygen at platinum is lower[13] in alkaline than in acid solutions. In other words, the active oxygen concentration is lower. Furthermore, oxidizing power in general is lower in alkaline than in neutral or acid solutions. This is to be concluded from the fact that many oxidations which take place readily in acid solution are either entirely prevented or proceed at a very much decreased rate when the solution is made alkaline.

It is noted that on starting the electrolysis both the potential of the anode and the efficiency are somewhat below their normal values. Both, however, steadily increase to a maximum with increasing time. This is entirely to be expected from the fact that reliable measurements of anodic overvoltage[14] always indicate a low concentration of active oxygen during the first few moments of oxygen discharge.

[12] Oechsli: *loc. cit.*, p. 817.
[13] Smale: Zeit. phys. Chem., **14**, 577 (1894).
[14] Foerster and Piguet: Zeit. für Elektrochem., **10**, 714 (1904).

Finally, on substituting an anode of platinized platinum for one of polished platinum, other conditions remaining constant, we find a notable decrease in anodic efficiency. This, once more, is satisfactorily explained from our viewpoint, since the work of Coehn and Osaka[15] interpreted from the viewpoint which we have taken shows that at a given current density we must have a lower concentration of active oxygen at a platinized anode than at one of smooth platinum. Their results[16] gave for the potential of oxygen at smooth platinum + 1.39 volts, and at platinized platinum + 1.19 volts.

From what has been said above, it becomes evident that we can satisfactorily account for the anodic formation of perchlorate without assuming anything at all about the liberation of the chlorate ion by considering that the oxidation is dependent only upon the presence at the anode of a sufficient concentration of active oxygen. It has been satisfactorily shown that this concentration corresponds to an anodic potential far below that required for liberation of gaseous oxygen and nearly as far below that required for the liberation of the chlorate ion, if we are to accept for this the values given by the best measurements available.

Although it may be readily admitted that the potential of the anode during the electrolysis of a chlorate solution is at all times probably above that necessary for chlorate discharge, it must be kept in mind that these reactions will not take place as long as we have chlorate present in sufficient concentration. This follows since it has been shown that the direct oxidation of the ClO_3 is the more easily accomplished process; that is, the one requiring the lowest potential, and as such will take place first. This does not mean that the oxidation will take place under all conditions with high efficiency since we have seen that those factors which unfavorably affect this reaction are exactly those which tend to lower the concentration of active oxygen at the electrode. The direct result of this decrease is a decrease in its ability to oxidize chlorate and a corresponding increase in the ease of oxygen evolution and the consequent drop in current efficiency with respect to perchlorate formation.

[15] Zeit. anorg. Chem., **34**, 86 (1903).

[16] The measurements given by them were made against a normal hydrogen electrode, but for the sake of consistency in this paper these have been converted to the normal calomel electrode values.

EXPERIMENTAL.

Although the theory outlined above is well supported by known facts, it seemed desirable to have independent proof of the fact that chlorates may be directly oxidized to perchlorates by chemical means and under conditions such that the liberation of the ClO_3 ion cannot be assumed.

We have evidence that this is true in the fact that chlorates when heated to moderate temperatures produce perchlorates, one portion of the chlorate furnishing oxygen for the oxidation of another portion; a reaction which may be represented by:

$$4NaClO_3 = NaCl + 3NaClO_4.$$

The possibility of a direct oxidation was even more strikingly shown by Fowler and Grant.[17] They found on heating chlorate with silver oxide that the chlorate was completely converted to perchlorate without the loss of oxygen, metallic silver being the other product.

It was desired, however, to show that the oxidation could be brought about in an aqueous solution and for this purpose several oxidizing agents were selected as the most useful and their action on sodium chlorate investigated as described below.

Methods of Analysis.

The method used for determining the amount of the various chlorine acids in the presence of each other was essentially that described by Treadwell-Hall[18] and is briefly as follows: In a solution containing chlorides, chlorates and perchlorates, or the corresponding free acids, the amount of chlorine as chloride was determined directly by titration of one sample (1). A separate portion (2) titrated, after reduction with ferrous sulphate with an excess of dilute sulphuric acid, gave the amount of chlorine as chlorate plus that as chloride. A third portion (3) of the solution after evaporation to dryness with sodium carbonate was fused in a tall platinum crucible, the mouth being closed by a plug of loosely packed asbestos fibre. This sample showed the total amount of chlorine present in all forms. The amount of chlorine present in the original solution is, then, shown by (1),

[17] Jour. Chem. Soc., **57**, 272 (1890).
[18] Analytical Chemistry, p. 463 (1911).

that as chlorate by the difference between that found in (2) and (1), and that present as perchlorate by the difference between the amount shown by (3) and (2).

The amount of chlorine in these samples was in all cases determined[19] by addition of an excess of tenth normal silver nitrate solution, filtering off the precipitated silver chloride and titrating the excess silver nitrate with a tenth normal solution of ammonium sulphocyanate, using ammonium ferric alum as indicator. This method was found to be rapid and gave consistent and very accurate results. Duplicate samples containing 0.3 gram chlorine frequently gave results differing by only 0.3 milligram.

In addition to the quantitative determination all solutions were examined for the presence of perchlorates by the micro-chemical test described by van Breukeleveen.[20]

Experiments with Persulphate.

The first oxidizing agent studied was sodium persulphate. This is commonly considered as a very powerful oxidizing agent and it seemed probable that it might convert chlorate to perchlorate even in aqueous solution. This was established as true by the following experiments.

Preliminary Experiment: A solution containing about 5 percent of sodium chlorate was boiled for ten minutes with an excess of sodium persulphate. After evaporation to dryness concentrated hydrochloric acid was added and the solution again evaporated, on a water bath, to convert all remaining chlorate to chloride. After dissolving the residue in water, silver nitrate was added until all chloride present was removed. After filtering the solution was evaporated, the residue fused with sodium carbonate, dissolved in dilute nitric acid and silver nitrate added. A heavy precipitate of silver chloride indicated that a portion of the chlorate originally present had been converted to perchlorate.

Experiments 8-12: One-gram portions of sodium chlorate, representing 0.3324 gram chlorine as chlorate, were boiled with solutions of sodium persulphate; the conditions being as shown below. In all cases a considerable oxidation to perchlorate was found. Tests of the several solutions for chlorides, after boiling

[19] Sutton: Volumetric Analysis, 9th Ed., p. 172.
[20] Rec. Trav. chim. Pay-Bas., **17**, 94 (1898).

with persulphate, showed the absence of chlorine in this form. We have to deal with chlorine as chlorate and perchlorate only. The latter was determined by difference, as in the first experiments.

	8	9	10	11	12
Chlorine (as chlorate) taken...	0.3324	0.3324	0.3324	0.3324	0.3324
Water—cc.	100	100	100	25	25
Sodium persulphate (grams) ..	10	10	10	10	10
Length of time heated (minutes)	30	30	60	30	30
Chlorine (as chlorate) found...	0.2710	0.2705	0.2736	0.2730	0.2751
Percentage oxidized to perchlorate	18.47	18.32	17.69	17.87	17.24

While these experiments showed in a satisfactory manner that chlorate may be oxidized to perchlorate by means of persulphate, it was desired, if possible, to establish conditions under which the oxidation would take place more efficiently, since it was noted that a large amount of oxygen was evolved during the reaction in the previous experiments. It has been pointed out[21] that the presence of silver salts seems to affect favorably the oxidizing power of persulphates, many substances being easily oxidized in this manner which are scarcely affected by persulphate alone.

Experiment 26: One cc. of tenth normal silver nitrate was added to a solution containing one gram sodium chlorate in 25 cc., representing 0.3324 gms. Cl, and 10 gms. sodium persulphate. Boiled one-half hour.

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment	0.2565 grams
Oxidized to perchlorate	0.0759 grams
Oxidized to perchlorate	22.83 percent

This experiment confirmed the fact that the presence of even small amounts of silver salts increased the oxidizing power of persulphates. Since this phenomenon has been ascribed to the fact that silver salts catalytically increase the velocity with which persulphate decomposes, and since this decomposition may be represented by:

$$Na_2S_2O_8 + H_2O = 2NaHSO_4 + O$$

it seemed probable that under conditions such that the sulphate ion would be removed from the sphere of reaction as fast as

[21] Price: Per Acids and their Salts, p. 35 (1912).

formed, the velocity of decomposition and the oxidizing power might be favorably affected. This was confirmed as follows:

Experiment 31: A solution, containing in 100 cc., one gram sodium chlorate, 10 grams sodium persulphate and 13 grams barium oxide was boiled for 30 minutes. After removal of the barium sulphate, an analysis gave the following results:

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment	0.2202 grams
Oxidized to perchlorate	0.1122 grams
Oxidized to perchlorate	33.75 percent

Although it seemed certain that in the previous experiments the oxidation was due solely to the persulphate present, the statement is frequently made that dilute solution of chloric acid or weakly acid solutions of chlorates are somewhat oxidized to perchlorate on boiling. To determine whether this was true for the conditions employed in the experiments described two solutions were made up containing in 25 and 100 cc. respectively an amount of sulphuric acid and of sodium sulphate corresponding approximately to the end products of decomposition of 10 grams sodium persulphate; that is, 6 grams sodium sulphate and 2.1 cc. concentrated sulphuric acid. To each of these one gram sodium chlorate was added and the solution boiled for 15 minutes. Neither the usual analysis nor the micro-chemical test showed the presence of perchlorate in either solution after this treatment. This shows conclusively that the oxidation obtained in experiments previously described is to be assigned to the sodium persulphate.

In all cases described the micro-chemical test[22] showed the presence of considerable quantities of perchlorate. It seemed desirable, however, to determine analytically the quantity of perchlorate present. This was done as follows:

Experiment 40: One gram sodium chlorate, containing 0.3305 gram Cl as chlorate, added to 10 grams sodium persulphate in 25 cc. water. Boiled 30 minutes.

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorine) found after treatment	0.2886 grams
Total chlorine found after treatment	0.3312 grams
Oxidized to perchlorate	0.0626 grams
Oxidized to perchlorate	18.94 percent

[22] Van Breukeleveen, *loc. cit.*

These experiments establish satisfactorily that chlorate can be oxidized to perchlorate by means of sodium persulphate.

Experiments with Ozone.

Although the action of ozonized oxygen on solutions of chlorates was investigated by Oechsli,[23] the result of his experiments is hardly conclusive, since one case in which a 2.5 percent sodium chlorate solution was saturated with ozonized oxygen for 8 hours, showed a decrease of 1.2 percent in the chlorate content. A following experiment in which free chloric acid was substituted for the sodium chlorate, gave a decrease of 0.34 percent in chlorate as a result of the treatment with ozone. The conclusion reached, however, was "das eine Oxydation des ClO_3 Ions durch ein etwa 6 Volumprozent Ozon enthaltendes Gas nicht bewirkt werden kann."

It seemed desirable, therefore, to carry on experiments with ozone in order to determine whether a larger proportion of the chlorate might not be oxidized by this means.

Experiment 25: Ozonized oxygen for this experiment was generated by passing dry oxygen through a Siemen ozonizer, the high tension current being supplied by a 10,000 volt transformer of 1 KVA capacity. The gas thus generated was bubbled through the chlorate solution contained in a large test tube, the length of the experiment being 19 hours and the temperature of the solution 22°. The solution contained 1 gram sodium chlorate and 1 cc. sulphuric acid (Sp. gr. 1.82) in 25 cc.

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment	0.3298 grams
Oxidized to perchlorate	0.0026 grams
Oxidized to perchlorate	0.78 percent

Since it is known that silver oxide decomposes ozone catalytically, it was thought that the presence of this substance might have a favorable effect on the oxidizing power. This seemed especially probable in view of the increased oxidation obtained with persulphate through the presence of silver salt.

Experiment 28: Solution consisted of one gram sodium chlorate, 1 cc. of normal nitric acid, 0.10 gram silver oxide and 25 cc.

[23] *Loc. cit.*, p. 821.

water. Ozonized oxygen was bubbled through the solution for 20 hours, the temperature of solution being 22° C. Results of analysis follow:

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment	0.3262 grams
Oxidized to perchlorate	0.0062 grams
Oxidized to perchlorate	1.86 percent

Experiment 32: The solution used was the same as in the previous experiment but was maintained at 100° C. Ozonized ozygen was passed through the solution for 5 hours. Result of analysis follows:

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment	0.3301 grams
Oxidized to perchlorate	0.0023 grams
Oxidized to perchlorate	0.69 percent

Although no attempt was made in the previous experiments to regulate the ozone concentration of the ozonized oxygen used, it was known to be about 7 percent by volume. It seemed probable that a gas with higher ozone concentration might be more effective in obtaining the desired oxidation. An apparatus was therefore constructed which was capable of producing oxygen containing a very high percentage of ozone. The ozone was produced by electrolysis of sulphuric acid solutions at low temperatures. The apparatus employed was essentially a modification of that described by Fischer and Massenay.[24]

No attempt was made to control the concentration of ozone produced by this apparatus, but it continuously furnished a gas of very much higher content than that from the Siemens tube. One analysis showed a concentration of 21 percent ozone by volume.

Experiments 38 and 39: Solutions containing one gram sodium chlorate and 2 cc. sulphuric acid (Sp. gr. 1.82) in 25 cc. water were used and were maintained at 100° by means of water bath. Ozonized oxygen produced by the apparatus described was allowed to bubble through these solutions for two hours. As in the previous cases a slight oxidation of the chlorate was obtained.

[24] Zeit. anorg. Chem., **52**, 202, 229 (1907).

Analysis.

	No. 38	No. 39
Chlorine (as chlorate) taken	0.3324	0.3324
Chlorine (as chlorate) found after treatment	0.3300	0.3296
Oxidized to perchlorate	0.0024	0.0028
Oxidized to perchlorate	0.72%	0.82%

The experiments with ozone show, therefore, that while ozone is capable of oxidizing acid solutions of chlorates, the oxidation it not at all efficient. In all cases described the amount of ozone used was in excess of the theoretical amount necessary to oxidize all chlorate present. It may be pointed out that while the amount oxidized is small it is nevertheless certain that perchlorate was produced since the micro-chemical test showed, unquestionably, the presence of perchlorate in all solutions after treatment with ozone.

Since acid solutions of permanganates are known to be strong oxidizing agents, this was the next material studied.

Experiment 45: A solution containing one gram sodium chlorate, 1 cc. sulphuric acid (Sp. gr. 1.82) and one gram potassium permanganate in 100 cc. water was boiled for 30 minutes. The solution showed no perchlorate present.

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment	0.3326 grams

This experiment shows that acid solutions of potassium permanganate will not oxidize chlorate to perchlorate.

The next oxidizing agent studied was aqueous sodium peroxide.

Experiment 46: A solution containing one gram sodium chlorate and 10 grams sodium peroxide in 25 cc. was boiled for 15 minutes. After cooling and diluting to 100 cc. the solution was acidified with dilute nitric acid.

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment	0.3317 grams

The slight discrepancy noted here between the amount of chlorate taken and that found after treatment is probably to be regarded as experimental error since the micro-chemical test used failed to show the presence of perchlorate. The amount represented by the difference in the two chlorine determinations is

probably within the experimental error in this case since the presence of large amounts of sodium salts in the solution made the analysis somewhat less accurate than in previous cases.

Experiments with Hydrogen Peroxide.

Hydrogen peroxide is probably to be considered as one of the strongest of oxidizing agents since its decomposition must be accomplished by the generation of atomic or active oxygen:

$$H_2O_2 \rightarrow H_2O + O_1.$$

Although not commonly so considered it should be a stronger oxidizing agent than ozone since the decomposition of the latter is represented by:

$$O_3 \rightarrow O_2 + O_1.$$

The concentration of active oxygen in the case of the hydrogen peroxide is thus seen to be much higher. Consequently its oxidizing power must be correspondingly greater.

The action of hydrogen peroxide on chlorate solutions was therefore next investigated.

Alkaline solutions of hydrogen peroxide were used as oxidizing agents. A solution containing one gram sodium chlorate and 1 cc. ammonium hydroxide (Sp. gr. 0.90) in 15 cc. perhydrol was boiled for 30 minutes. Analysis of the solution gave the following results:

Analysis.

Chlorine (as chlorate) taken	0.3305 grams
Chlorine (as chlorate) found after treatment	0.3298 grams

No perchlorate could be found in the solution by microscopic test. The experiment therefore shows that alkaline hydrogen peroxide is not a sufficiently powerful oxidizing agent to convert chlorates to perchlorates.

Experiment 47: One gram of sodium chlorate was dissolved in 15 cc. perhydrol (Merck's 30 percent) and the solution evaporated to dryness on the water bath. The residue was dissolved in a second 15 cc. portion of perhydrol and again brought to dryness. After dissolving the residue in water the following analysis was obtained:

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chlorate) found after treatment	0.3327 grams

This experiment shows that chlorate in neutral solutions is not oxidized to perchlorate by 30 percent hydrogen peroxide.

It is undoubtedly true that oxidizing agents, in general, are more powerful in the presence of acid than in neutral or alkaline solutions. Therefore it was decided to investigate the action of hydrogen peroxide on acid solutions of chlorates. Some work has been done along this line by Tanatar[25] who investigated the action of hydrogen peroxide on halogen oxy-acids. He found that hydrogen peroxide had no effect on either neutral or acid solutions of chlorates, while bromates were quickly reduced to bromide with evolution of some bromine. These conclusions are certainly in error in so far as they state that acid chlorate solutions are unaffected by hydrogen peroxide. This will be seen from the following experiments:

Experiment 48: One gram sodium chlorate was dissolved in 25 cc. of 30 percent hydrogen peroxide which had previously been acidified by 1 cc. sulphuric acid (Sp. gr. 1.82). The solution was boiled for one hour. Soon after the solution had reached the boiling point a yellow gas was evolved. This was at first thought to be chlorine but more careful examination showed it to be a mixture of chlorine dioxide and chlorine. The microchemical test showed the presence of perchlorate in the solution and analysis gave the following results:

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chloride) found after treatment	0.2916 grams
Chlorine (as chlorate) found after treatment	0.0030 grams
Total chlorine found after treatment	0.2927 grams

This experiment shows that chlorate, through the action of acid solutions of hydrogen peroxide, is largely converted to chloride. A considerable amount of chlorine and chlorine dioxide is evolved at the same time.

Experiment 49: The conditions in this experiment were the same as in the previous case with the exception that 3 percent

[25] Ber., **32**, 1013 (1899).

hydrogen peroxide was used. The solution was boiled for 12 hours.

Analysis.

Chlorine (as chlorate) taken	0.3324 grams
Chlorine (as chloride) found after treatment	0.0122 grams
Chlorine (as chlorate) found after treatment	0.3162 grams

This experiment, again, shows that by the action of acid hydrogen peroxide solutions on chloride we have apparent reduction to chloride. This was confirmed by a series of experiments which all gave results similar to those described above.

It now became necessary to account for the *apparent* reducing action which hydrogen peroxide exerted on acid chlorate solutions. The fact that chlorine and chlorine dioxide were set free during this reaction caused no difficulty. The presence of a small amount of hydrochloric acid in the solution would be sufficient to account for this, since it is known that hydrochloric acid solutions rapidly decompose chlorate, particularly when heated to 80°. This decomposition may be represented by

$$HClO_3 + HCl \rightarrow H_2O + ClO_2 + Cl.$$

It seemed certain, therefore, that the main reaction with which we were dealing was an apparent reduction of chloric to hydrochloric acid, and that the evolution of chlorine and chlorine dioxide was to be considered as a secondary reaction due to the action of hydrochloric acid on chlorate, which still remained undecomposed.

To account for the apparent reducing action shown here by hydrogen peroxide several possibilities presented themselves. It seemed improbable that so strong an oxidizing agent as hydrogen peroxide was here acting as a reducing agent, especially in view of the fact that many, if not all, of the apparent reductions accomplished by hydrogen peroxide are in reality the result of oxidations to higher instable oxides[26] which immediately decompose if the experiment is conducted under ordinary conditions. Applying this idea to the case in question it was considered possible that the chloric acid was oxidized by hydrogen peroxide to a higher form, which was unstable under ordinary conditions. Since the acid next higher than chloric acid is perchloric acid

[26] This will be discussed more fully in a later paper.

and this was shown to be perfectly stable under the conditions existing in the experiments it was necessary to assume the formation of an acid still higher than perchloric. The further assumption necessary was that this hypothetical higher acid would decompose spontaneously with the liberation of oxygen and formation of hydrochloric acid.

Assuming for the moment the existence of this compound it seemed highly probable that during its formation from chloric acid we would pass through the perchlorate stage, or, in other words, that it should be formed equally well from perchloric acid. A preliminary experiment showed, however, that this theory was untenable. A 5 percent solution of potassium perchlorate acidified with sulphuric acid was added to an equal volume of 30 percent hydrogen peroxide and the whole boiled for 10 minutes. No chlorides were present in the solution after this treatment. This experiment is supported by the work of Tanatar[27] who found that perchloric acid is not affected by hydrogen peroxide. It became necessary, therefore, to abandon the position first taken.

The possibility next considered was the existence of a molecular compound between chloric acid and hydrogen peroxide. No assumptions were made as to the nature of this hypothetical compound, but for the time being it was considered analogous to the possible compounds between ferrous sulphate and hydrogen peroxide described by Mummery.[28] The hypothesis which we are now considering postulated, of course, that this compound $HClO_3 . x\, H_2O_2$ if existent, would decompose with formation of hydrochloric acid.

If this compound were actually formed on mixing solutions of chloric acid and hydrogen peroxide it seemed probable that its presence would be revealed by a measurable thermal change. Accordingly the heat of dilution of solutions of chloric acid with hydrogen peroxide was determined as follows:

Experiment 50: The apparatus used consisted of a silvered Dewar flask of about 200 cc. capacity, fitted with a stopper carrying a small funnel tube and a 100° thermometer, graduated in

[27] *Loc. cit.*
[28] Jour. Soc. Chem. Ind., **32**, 889 (1913).

0.1°. The stopper was also cut away at one side to permit the introduction of a glass stirring rod.

Twenty cc. of a 5 percent chloric acid solution was introduced into the flask and the temperature allowed to become constant. 5 cc. 30 percent hydrogen peroxide solution were then brought to the same temperature and introduced into the flask. The temperature of the mixture rose rapidly and reached a value where it remained constant for several minutes. The thermal effect on diluting 20 cc. of 5 percent chloric acid with 5 cc. of water was next determined, the procedure being exactly similar to that used in the previous case. The data obtained was as follows:

Initial temperature of chloric acid	24.70°
Initial temperature of hydrogen peroxide	24.70°
Maximum temperature of mixture	24.95°
Rise in temperature of mixture	0.25°
Initial temperature of chloric acid	24.55°
Initial temperature of water	24.55°
Maximum temperature of mixture	24.80°
Rise in temperature of mixture	0.25°

These experiments are sufficient to indicate that there is little possibility of the formation, at room temperature, of a compound of chloric acid and hydrogen peroxide. One possibility remained to be considered, however, before abandoning this hypothesis. It has been mentioned that the apparent reducing action of hydrogen peroxide on chloric acid does not become evident until a temperature of about 80° is reached. The possibility existed, therefore, that the intermediate compound just considered might be formed at a point somewhat above room temperature. If this were true the formation of the compound would be indicated by a break in the heating curve of a mixture of chloric acid and hydrogen peroxide. An investigation of the heating curve of a 5 percent chloric acid solution mixed with an equal volume of 30 percent hydrogen peroxide failed to show any break which would indicate the formation of a compound.

The conclusion was therefore reached that the *apparent* reduction of chlorate to chloride by hydrogen peroxide could not be assigned to the formation of an instable compound between the two.

The most satisfactory explanation of this phenomenon, however, was found in the fact that in a dilute solution of chloric

acid we have a small amount of chlorine liberated through spontaneous decomposition of the acid. This chlorine, by its action on the hydrogen peroxide immediately forms hydrochloric acid.[29] The hydrochloric acid thus produced would, of course, immediately attack the remaining chlorate, the products of this reaction being hydrochloric acid, chlorine, chlorine dioxide, and oxygen. The reaction is therefore auto-catalytic, and a small amount of hydrochloric acid is sufficient to start the decomposition. It has been mentioned that the formation of chlorides in a solution of chloric acid and hydrogen peroxide, does not begin to be appreciable until the temperature is raised to about 80°. This is in accord with the work of Sand,[30] who investigated the reaction between chloric acid and hydrochloric acid. He found that the velocity of the reaction became appreciable at temperatures above 70°.

This explanation of the apparent reducing action of hydrogen peroxide in chloric acid has the advantage that it makes no assumption whatever but uses only well-known facts to account for the phenomenon. There is scarcely room for doubt that the explanation put forward represents the true mechanism of the reaction. It also shows that hydrogen peroxide does not here act as a reducing agent, in the true sense of the term.

Experiments with Activated Oxygen.

The fact that oxygen is activated or ionized by ultra-violet light rays is well established.[31] In this condition it is a very powerful oxidizing agent, probably stronger than either ozone or hydrogen peroxide. The action of activated oxygen on chloric acid was therefore investigated.

It is frequently stated that solutions of chloric acid are slowly oxidized on standing in sunlight. While this is probably true the necessity for the presence of oxygen has not been recognized.

A solution was made up containing 0.4784 gram sodium chlorate and 0.25 cc. sulphuric acid (Sp. gr. 1.820) in 45 cc. This represented 0.1582 gram chlorine as chlorate. The solution was placed in a transparent quartz flask and a neutral atmosphere maintained by continuously passing in nitrogen which had been

[29] Fairley: Jour. Chem. Soc., **31**, 22 (1877).
[30] Zeit. phys. Chem., **50**, 465 (1904).
[31] Sheppard, Photo-chemistry, p. 253 (1914).

freed from traces of oxygen by washing with alkaline pyrogallol solution. Ultra-violet light was obtained by means of a Cooper Hewitt quartz tube mercury arc lamp, the flask containing the solution being suspended about 5 cm. from the lamp. The experiment continued for 28 hours. No oxidation of the chlorate took place, as is shown by the analysis.

Analysis.

Chlorine (as chlorate) taken	0.1582 grams
Chlorine (as chlorate) found after experiment	0.1580 grams

This experiment shows conclusively that, in the absence of oxygen, dilute chloric acid solutions are not photo-chemically oxidized to any appreciable extent.

The next experiment was similar to the preceding one, except that oxygen was continuously bubbled through the solution. The flask held 50 cc. of solution containing 1.000 gram of sodium chlorate and 0.50 cc. sulphuric acid (Sp. gr. 1.820). This represents 0.3305 gram chlorine as chlorate. The solution was subjected to the action of the ultra-violet rays for 8 hours. After the treatment, the micro-chemical test showed perchlorate to be present. This was confirmed by analysis.

Analysis.

Chlorine (as chlorate) taken	0.3305 grams
Chlorine (as chlorate) found after experiment	0.3269 grams
Oxidized to perchlorate	0.0036 grams
Oxidized to perchlorate	1.09 percent

It was desired to determine whether more of the chlorate could be oxidized by longer treatment with the activated oxygen.

Accordingly, a solution of sodium chlorate was made up and found, by analysis, to contain 0.1172 gram in 10 cc. The solution was acidified slightly (0.5 percent) with sulphuric acid. The other conditions being as in previous experiments the solution was subjected to the ultra-violet rays, oxygen being continuously bubbled through. 10 cc. samples, for analysis, were withdrawn at regular intervals. The results follow:

Time elapsed (hours)	Sodium chlorate found per 10 cc. solution
0	0.1172
24	0.1158
72	0.1160
96	0.1157

It will be noted that during the first 24 hours a small amount of the chlorate was oxidized. This represents about 1.1 percent of the total amount present. During the remaining time no further oxidation took place. It will also be noted that these results are practically identical with those obtained when ozonized oxygen was used as the oxidizing agent. It is probable that we have only a very low concentration of active oxygen in both cases and that it is not at all comparable, in degree, to that present at the anode during electrolysis. Consequently it is necessary to assume that, using active oxygen in these low concentrations, an equilibrium of some kind is established when about 1 percent of the chlorate present has been oxidized. It seems very probable that if this concentration of active oxygen be increased a further oxidation would result.

It is held, however, that the conditions maintained in the above experiments duplicate (qualitatively) those existing at the anode during chlorate electrolysis and show that perchlorate can be formed by the direct addition of oxygen to the chlorate radicle.

CONCLUSIONS.

1. Chlorate may be oxidized to perchlorate by persulphuric acid, ozone, and hydrogen peroxide in acid solutions.

2. In the case of hydrogen peroxide the hydrochloric acid formed interferes with the reaction.

3. This oxidation may also be carried on with oxygen activated by ultra-violet light.

4. The reaction is considered to take place according to:

$$HClO_3 + O_1 = HClO_4$$

the quantity of oxidation depending on the concentration of active oxygen present.

5. Since active oxygen chemically produced oxidizes chloric acid to perchloric acid and since active oxygen is formed at the anode it follows that the electrochemical formation of perchlorate is the result of direct oxidation.

6. Perchlorate is formed at the anode at a potential, far below that necessary for the continuous discharge of any ion present in the solution.

7. The conditions realized in the experiments described above duplicate, qualitatively, those existing at the anode during electrolysis.

Ithaca, New York.

DISCUSSION.

PRESIDENT ADDICKS: The experiments on the oxidizing effect of oxygen activated by ultra-violet light remind me of work I was interested in several years ago in connection with the recovery of selenium from flue dust. The selenium was leached out using $KClO_3$ as an oxidizing agent in shallow porcelain pans in the open air. It was found that the yield was much greater on sunny days than on cloudy ones.

C. W. BENNETT (*Communicated*): We have been unable to bring about the breaking down of potassium chlorate with ultra-violet light. It is probable that the increased efficiency on sunny days is brought about through oxidation of the metal by activated oxygen, the potential of which is sufficiently raised by the presence of the chlorate.

A paper read before the New York Section of the American Electrochemical Society, in Joint Session with the New York Sections of the American Chemical Society and the Society of Chemical Industry, on February 11, 1916. Called up for discussion at the Twenty-ninth General Meeting of the Society in Washington, D. C., April 27-29, 1916.

ELECTROLYTIC ZINC.

By W. R. Ingalls.

If in responding to a request that I contribute something on the subject of electrolytic zinc I repeat to a considerable extent what has already been printed in the "Engineering and Mining Journal," I must plead in extenuation that I am able to add but little to what I have already said in that publication.

Without any doubt, the most important thing in the metallurgy of zinc in 1915 was the inauguration of electrolytic zinc production direct from ore on a large experimental, even a commercial, scale at several places, the most important of these being at Anaconda, Mont., where the production of electrolytic spelter at the rate of about 5 tons per day was begun. The results are considered so favorable that the Anaconda company has commenced the erection at Great Falls, Mont., of a plant capable of producing 35,000 tons of electrolytic spelter per annum. With regard to the nature of the Anaconda process, Mr. Laist, who is responsible for it, has written me as follows:

"I can hardly claim that we have accomplished anything especially new in this line, except insofar as we have done on a somewhat larger scale what had often been done before by others in the laboratory and in a smaller way. Briefly, the process consists of concentrating the zinc ore, preferably by flotation, so as to make a concentrate with as little insoluble matter as possible and as rich in zinc as the nature of the ore allows. This concentrate is roasted in two of the furnaces of our copper-leaching plant, so as to produce a calcine containing from 2 to 3 percent sulphur, most of which is present as sulphate sulphur. The temperature is not allowed to exceed 1,350°F. (732°C.), under which conditions the formation of zinc ferrite is not pronounced.

"The calcine, after cooling, is treated with a solution containing

sulphuric acid, which dissolves the zinc and a little of the iron. A small amount of manganese dioxide is added for the purpose of oxidizing the iron, which is then precipitated by means of a small amount of powdered limestone. Any arsenic or antimony is carried down by the precipitated ferric hydroxide. The resulting solution contains nothing but zinc, cadmium and copper, and is separated from the residue by filtration. The residue contains the lead, silver and gold and part of the copper originally present. The solution is treated with metallic zinc to precipitate the copper and cadmium, and is then pumped through a clarifying filter-press into a storage tank, from which it goes to the electrolytic cells. The cell room contains 42 tanks, which are in no way different from those commonly used for copper refining. Here the zinc is deposited on aluminum plates.

"The solution from the cells contains sulphuric acid and is used for leaching a fresh charge. The zinc deposits on the aluminum plates are stripped off every 48 hr. and sent to the melting furnace. At the present time we are making about five tons of zinc per day of a high degree of purity."

I will add to this that the leaching is performed in Pachuca tanks, the lixiviant being spent electrolyte plus the quantity of fresh acid required. The anodes of the electrolytic cells are of pure lead. The solution is electrolyzed at a current density of 20 to 30 amperes per square foot (220 to 330 per square m.) of cathode surface, the general practice being about 23 (250) amperes. The voltage drop per cell varies from 3.8 volts at the head cell of the series (21 cells in cascade series) to 3.4 volts in the tail cell. Current efficiency is from 93 to 94 percent.

Apart from the Anaconda work, the most ambitious plans carried on in 1915 were those of the Consolidated Mining and Smelting Co. of Canada, which continued the experimental work begun several years ago. In the last official report of this company it is stated that spelter of good grade has been produced at the rate of 1,000 lb. (453 kg.) per day from Sullivan mine ore, and that the results were sufficiently promising to warrant the building of a plant capable of producing 25 to 35 tons of spelter daily. Construction of this plant is well advanced, and it is expected to be in operation early in 1916.

Electrolytic zinc was also produced in 1915 on an experimental scale by the Electro Zinc Co. at Welland, Ont., while some work in this line was done at Keokuk, Iowa, and at Bully Hill, Calif., and there were one or two other operations (one of these employing the Isherwood process) that may not yet be mentioned publicly. The work at Welland is unique in that the dissolving of the zinc and the electrolysis of the solution is performed in the same vat, the cathodes being enclosed within canvas bags. All of the other work, so far as I know, is being done on lines similar to those at Anaconda.

Before going any further, let it be well fixed in the mind that the conditions that have existed in the zinc industry during the last year are not only unprecedented but also it is certain that they cannot be otherwise than ephemeral. They have been due to a shortage of metallurgical capacity, not of ore in the least degree, and that shortage is being reduced with extraordinary rapidity. In the meanwhile, however, there has naturally been a huge metallurgical margin—even $60 per ton of ore against a normal of about $15—in the manufacture of common spelter, and with such a margin it has been good sense not only to commit metallurgical crimes but also to institute new processes that would not ordinarily be profitable. In the manufacture of high-grade spelter the margin has been much higher, so much so that the possibility of it would two years ago have been considered nothing less than preposterous.

The electrometallurgy of zinc is no new thing. The electrolytic refining of impure spelter was tried on a large scale by Nahnsen in Upper Silesia in the nineties, the hydrometallurgical-electrometallurgical treatment of zinc ore was essayed disastrously by Ashcroft at Cockle Creek, N. S. W., in a works costing about one million dollars. Dr. Hoepfner developed a process that was put into use at Führfort on the Rhine and at the works of Brunner, Mond & Co., at Winnington in England. At the former it was abandoned after a short time; at the latter it has been continued through a long series of years, making a few hundred tons of spelter annually, and is in use at the present time. The electrometallurgy of zinc has therefore a commercial history of respectable antiquity.

In the early days of the art, both commercial and experimental, difficulty was experienced in obtaining dense deposits on the cathodes, spongy zinc being a stumbling block, but while this matter required some study for its mastery, it was manifest that the real difficulties of this process were the getting of zinc into solution rather than out of it, and the large amount of power required for zinc precipitation.

With regard to the former point, I refer to the formation of insoluble ferrite of zinc in roasting, with the consequence of relatively low extraction of zinc. That is experienced in the case of many, perhaps most, ores that it is desired to treat. To illustrate, roasted Joplin blende may be leached with sulphuric acid so as to cause it to give up 97 or 98 percent of its zinc, the residue being a white silica sand, but nobody wants to treat Joplin ore by a hydrometallurgical process, for the reason that it would be less economical than ordinary smelting. On the other hand, certain mixed ores, high in iron, like those of Leadville, Colo., may give up only about 65 percent of their zinc. So low an extraction would in itself be prohibitive in most circumstances in ordinary times. It is possible that the roasting might be conducted in such a way as to steer clear between the Scylla of zinc ferrite on the one hand and the Charybdis of undecomposed zinc sulphide on the other hand, but that question has not been investigated with definite results, so far as I know. With regard to the high power required for the electrolysis of zinc solutions with insoluble anodes, the expense of it, when imposed upon the cost of roasting, leaching, remelting cathodes, reworking between-products, etc., is likely to make the cost of hydrometallurgical-electrometallurgical zinc extraction too high to be ordinarily considered.

I have, therefore, repeatedly expressed the opinion that metallurgical processes of this sort were unlikely to be successful commercially, unless: (1) Exceptionally cheap hydroelectric power, such as the $6 or $7 per annual horsepower of Norway and Sweden were available; or (2) unless use could be made of the anode reaction, such as the liberation of chlorine by the electrolysis of a chloride solution and the employment of it for some chemical manufacture, as at Winnington, England; or (3) unless certain especially favorable conditions otherwise existed. By the

last I mean such things as high grade of the run-of-mine ore, a kind of ore that will give up a high percentage of zinc by lixiviation with sulphuric acid, an ore high in silver, and possibly lead. These points are almost determinative. In the pyrometallurgy of zinc the extraction of silver is, perhaps, about 65 percent. In the hydrometallurgy of zinc it ought to be upward of 90 percent, perhaps as high as 95 percent. The situation with respect to lead is somewhat similar. It is needless to dwell upon the importance of this in the cases of ore exceptionally high in silver.

Now, in the treatment of the Butte ore at Anaconda, about all of the favorable conditions that I have enumerated under the third head exist. The ore raised from the mine is of rather high grade, it is of a character that enables 90 percent of the zinc, or more, to be extracted by sulphuric acid lixiviation, and as zinc ores go, it is exceptionally high in silver (the concentrated ore going 20 oz. silver per ton (0.07 percent) or thereabouts). Moreover, the Anaconda company is introducing zinc extraction in connection with its other great metallurgical work, thus dividing general and administrative expenses, etc. It is able to obtain moderately cheap power at Great Falls, and finally, what is not least in importance, it possesses about the best metallurgical organization of any concern in the United States, and is instituting this new process at a time when there ought to be commercial profit in spite of any imaginable infantile disorders. I am not free to communicate such figures respecting the Anaconda results as I know, but I may say that the Anaconda management is thoroughly aware of the exceptional conditions existing in the zinc industry at present and is nevertheless of the opinion that with its peculiarly favorable circumstances it can continue the production of electrolytic zinc in competition with everybody else in the normal times, or even in the hard times that may be experienced after the termination of the war. The promise of the development of the hydrometallurgy-electrometallurgy of zinc as a commercial art on a large scale has, therefore, already become a prospect. There is to be such an art. The magnitude that it will attain, and its effect upon the zinc industry of the world, remain for the future to tell, but that it is going to have an early and important influence is not to be doubted.

Turning attention to some of the technical features of electrolytic zinc production, the conditions governing the electrolysis of zinc solutions were exhaustively treated by Dr. Victor Engelhardt in a paper read at the first general meeting of the Gesellschaft Deutscher Metallhütten- und Bergleute and published in *Metallurgie* a few years ago. A summary of Dr. Engelhardt's conclusions, together with some additional notes, was published by Prof. J. W. Richards in Transactions of the American Electrochemical Society (1914), **25**, 281-290. The ideas of Dr. Engelhardt, who is the chief engineer of the electrochemical division of the Siemens & Halske Company of Berlin, are exemplified in what are called the Siemens & Halske and Isherwood processes. However, in the late development of zinc electrolysis, "processes" and patents have played but slight part. With recent experimenters the matter of spongy zinc deposits appears to have been among the least of the difficulties. Mr. Keating succeeded several years ago in depositing smooth, solid zinc on his cathodes at Bully Hill, Cal., while as for Mr. Laist, he accomplished this part of the process as a matter of course, just as simply as if he were depositing copper, the necessary precautions as to purity of solution, etc., being naturally taken.

With regard to the grade of electrolytic zinc, high purity is easily obtained. This is something that is far more under control than in refining by fractional distillation. Lead ought not to go appreciably into solution at all, while iron, copper and cadmium, the other common impurities of spelter, are readily precipitated from the solution. The spelter first made at Anaconda was higher in cadmium than is permitted by the standard specifications for "high-grade." At that time zinc dust, more or less impure, was being used as the precipitant for cadmium. Running the clarified solution through a tube-mill filled with zinc balls corrected this and the grade of the spelter was then raised to upward of 99.9 percent. Brunner, Mond & Co. have been for many years guaranteeing their electrolytic spelter at 99.95 percent zinc, and there is no reason why the Anaconda spelter should not be made as good as that.

Is electrolytic zinc extraction going to revolutionize the metallurgy of zinc? Unqualifiedly, no. When the zinc industry returns to its normal status, conditions will be in the main as they were

before the war and the principles that I have previously stated will continue to obtain, with the difference that some people will have learned the details of the art, will have gone through the period of infantile mistakes in a time when almost any mistake was of no great consequence. By that time some of the concerns possessing exceptionally favorable conditions, Anaconda, if anybody, may be able to continue. Others will not.

However, there are certain new industrial features that can not yet be clearly estimated and may have a modifying effect upon this forecast. One of these relates to the matter of high grade zinc. Previous to the war, that class of spelter was produced in limited quantity and sold at a premium over common spelter of about 2.5 cents per lb. Inventors, promoters and others who talked about making such zinc were discouraged from reckoning upon the premium by the dictum that the market would not take any more than the then supply, which was indeed artificially limited, and that it was unsafe to count on anything but the price for common spelter. During the war high-grade spelter has fetched 40 cents per lb. and at times the demand for it has been insatiable. This demand has been especially in connection with the manufacture of ammunition and may be expected to cease with the war, but will the advertising that high grade spelter has had and the wider knowledge of its peculiar properties that has been acquired give it a more extensive use in the peaceful arts and a maintenance of the premium for it, that will be to the advantage of the electrolytic producer? Or, will it become a drug in the market, with entire disappearance of price differential? These are questions that nobody yet knows enough to answer reasonably.

Another new and uncertain factor is the bearing of the flotation process of ore concentration upon the metallurgy of zinc. I think that this had a good deal to do with the institution of the Anaconda work. About all metallurgical work is a sequence of steps of concentration and refining, treating the bulk of the ore by a cheap but wasteful process and delivering a concentrated product to a more costly but less wasteful process. Now, most experimenters in the hydrometallurgy and electrometallurgy of zinc heretofore have contemplated the application of a costly process to the run-of-mine ore. The flotation process has enabled ore to be concentrated at relatively small cost with but slight loss. Let it be

observed, therefore, that Mr. Laist is applying his costly process not to run-of-mine ore, but to a flotation concentrate in which about 90 percent of the zinc is concentrated in about one-fourth of the original weight. This is the new and important feature of recent zinc electrolytic work.

We must let our thoughts run a little further ahead. The treatment of flotation concentrate is one of the present troubles of the zinc smelter, owing to its excessive fineness, which produces difficulties that it would take me too long to describe. Yet the proportion of this class of ore that the zinc smelter is getting, is still relatively small. The supply of it is, however, bound to increase and when it becomes large, the troubles of the zinc smelter will really begin. Now the hydrometallurgist will have the same troubles up to and through the roasting of the ore, but he will be free from those that arise in the distillery. In so far he will have an advantage over his brother pyrometallurgist, but whether it will be a weighty advantage, I do not venture to offer an opinion.

Another thing that may help the hydrometallurgist is improvement in the method of roasting. Twenty-five years ago he used to talk about sulphate roasting. He did not in practice find that idea to work out as well as he expected. While he might be able to render 40 or 50 percent of the zinc soluble in water, he found there was too much undecomposed sulphide left behind after leaching with sulphuric acid. So then he said he would roast the ore completely, leach all the zinc with sulphuric acid and be done with it. To his surprise he found that much of the zinc had been rendered insoluble by the formation of zinc ferrite, if iron were present in the ore, as was almost always the case. The roasting of ferruginous blende in such a way as to convert all the zinc into sulphate and oxide, avoiding both sulphite and ferrite, which may perhaps be done by correct control of temperature, perhaps by some other control, is an interesting subject for investigation. Mr. Laist has given some attention to this by carefully limiting the temperature of his roasting furnace. However, I think that perhaps the danger of ferrite formation is not very great in the case of his ore. Anyway, I know that the danger is not very great in roasting some similar ore of Butte, without much regard to the matter of temperature.

DISCUSSION.

PRESIDENT ADDICKS: I am sorry Mr. Ingalls is not with us, as he has previously addressed us on this subject and presented reasons why electrolytic zinc plants could not be commercially successful, while in this paper he has been obliged to revise his former opinions and to admit that some of them are successful. I believe we have overlooked a commercial factor which will greatly extend the electrolyzing of zinc. It is self-evident in many cases that it does not pay, in treating Joplin ores, to go to the expense of electrolyzing when you do not get any more for the zinc. Up to recently there has not been any demand for any great quantities of very pure spelter, but now there is a good deal of it available. It is coming on the market as a special brand, which people are trying, and after a while they may be unwilling to pay extra for it. But the time will come when the spelter market is down, and the fellow with the special-brand product will sell his and the fellow with the ordinary product will not sell his. I think the electrolytic zinc has not only come, but will stay.

CARL HERING: At present there are many lead and copper ores in the West that are penalized for their contents of zinc; there is therefore an additional money factor in treating those ores, because one not only gets the zinc for nothing but is paid something for taking it out. I know of a process used in California, not mentioned in the paper, in which the original material is a waste product from a metallurgical operation; after the zinc has been taken out this product becomes valuable again.

J. W. RICHARDS: I agree with Mr. Addicks that the day of electrolytic zinc has come, and that electrolytic zinc produced from the ore, through means of solution and electro-deposition, is going to be a very large factor in the commercial zinc world. At the present time the Anaconda Company is building a plant to cost something like a million dollars, to produce 100 tons of zinc a day by this method. The state which we have been looking forward to for many years has practically arrived and the question is solved; many of the discussions before this Society have helped in solving the question.

I wish particularly to mention the work of Mr. Hansen, who made for the General Electric Company a large series of laboratory experiments and determined the conditions under which zinc could be deposited. His work, unfortunately, was not ready to be presented at this meeting.

President Addicks: One of the troubles has been to plate out zinc without using a diaphragm to prevent re-solution of the cathode in the free acid. The answer lies in getting absolutely pure cathodic zinc. Pure cathode zinc seems to be sufficiently immune from these troubles, even in the presence of the considerable amount of free sulphuric acid necessary to make the process commercial.

W. R. Ingalls: My friend Addicks errs in conveying the idea that I have reversed my opinion respecting the commercial prospects of electrolytic zinc extraction. Had I done so I should not hesitate to admit it, but anyone who will take the trouble to refer to my former expressions on the subject will find that I indicated the prospects of economical hydro-electrometallurgical zinc extraction as being limited to certain favorable conditions. Before anybody jumps to any conclusion to the contrary, he would best do some careful figuring. I admit freely that certain recent advances in the art of metallurgy have been favorable to the electrolytic process. Most important of these are the improved machinery for leaching, and especially the use of the flotation process, which gives a high-grade concentrate with which to work. I am not bold enough to prophesy what is going to be the effect upon the market for high-grade spelter; it may be that it will competitively displace common spelter, as Mr. Addicks foresees, but it may be also that it will have to be sold on equal terms with common spelter.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

REVIEW OF RECENT PROGRESS IN ELECTROLYTIC IRON.

By Oliver W. Storey.

Electrolytic iron, up to within the past few months, has been a laboratory rather than a commercial product, but recent developments show that it is another electrochemical achievement to take its place among the industries of this country. At least one of the large electrical concerns is turning out 1,000 pounds (453 kg.) of electrolytically refined iron per week with a probable increase to several times this output in the near future. The method used is that developed by Burgess[1] and later modified by Watts.[15] The electrolyte consists of 150 grams of $FeSO_4.7H_2O$, 75 grams $FeCl_2.4H_2O$, and 120 grams $(NH_4)_2SO_4$ per liter, with a specific gravity of 1.125 at 20° C. Ammonium oxalate is used as an addition agent. The anodes consist of bars of basic open-hearth steel. The deposit reaches a thickness of ⅜ to ½ inch (10 to 13 mm.) before it is necessary to remove the cathode.

While the electrolytic refining of iron is an infant industry at the present time it is well to remember that electrolytic zinc refining was at the same stage of development a year ago. Two years ago it was thought doubtful whether the problem could be solved except in the distant future. Now we read in the technical press of the erection of electrolytic zinc refineries whose cost will amount to several millions of dollars. With this example before us who can predict what the next few years will accomplish in the electro-deposition of iron?

Electrolytic iron is known to have been produced on a laboratory scale seventy years ago. As long ago as 1860 it was used for the plating of copper engravings for the printing of bank notes at the Imperial Mint at Petrograd, Russia. Until recently the only use to which electrolytic iron had been put was in the so-called "steel facing" of dies and electrotypes. Its hardness, which makes it suitable for such purposes, is due to hydrogen, either occluded or combined.

The commercial production of electrolytic iron as a source of pure iron received a decided impetus in 1904 when Burgess and Hambuechen[1] presented their paper on "Electrolytic Iron" before this Society. They showed that it was possible to refine iron by methods similar to those used for the refining of copper and obtain deposits up to one inch in thickness. The electrolyte consisted of a neutral ferrous sulphate solution containing some ammonium sulphate, while the anodes consisted of slabs of wrought or other soft iron. The current efficiency of deposition was near 100 percent and the resulting iron was of a high degree of purity, containing less than 0.10 percent and often under 0.03 percent of impurities. Over three tons of iron was refined and used for the production of over 1,000 "pure iron" alloys which were tested for their various properties.

After several years' experience upon a semi-commercial scale at the University of Wisconsin, Burgess[5] gives the following figures on the cost of commercial refining of mild steel, the product being an iron of a high degree of purity. He estimates the power cost per ton at $10, with power at a cent per kilowatt hour, one kilowatt hour producing two pounds (907 g.) of iron. The cost for labor, solution maintenance and fixed charges is estimated as equal to the power charge or $10. The anode material is assumed to be a mild steel costing $35. This would make the total cost about $55 per ton of refined iron. With power at ½ cent per kilowatt hour this cost would be reduced to $50.

In 1908 Cowper-Coles[2] described a method of making finished iron sheets and tubes by electrolytic methods from pig iron or from iron ore, using insoluble anodes when ore was used. The electrolyte was a 20 percent solution of sulpho-cresylic acid saturated with iron. The method differs from the Burgess process in that pig iron and iron ore are refined, and in a different choice of electrolyte. The process has not been used commercially though it is stated that works are being erected for the manufacture of electrolytic iron by this method.[3]

A detailed description of the Cowper-Coles process is given by Palmaer and Brinell.[4] They state that the electrolyte is a concentrated solution of ferrous chloride with additional organic compounds, such as the cresol-sulphonic acids, and enough iron oxide to make a sort of a gruel. The additional iron oxide is

used for reducing the acidity and polishing the iron which is deposited as a sheet on a rapidly revolving cathode at a temperature near the boiling point of water. The current density used is about 63 amperes per square foot (7 amp. per sq. dm.). The resulting product is brittle due to the presence of several tenths of one percent of hydrogen. It also contains about 0.50 percent of impurities, exclusive of hydrogen, while the pig iron used for anodes contains about 7 percent. The chlorine content of the deposited iron is high, probably being occluded electrolyte. This is a serious defect as it impairs the mechanical properties and promotes rusting. The figures given by Palmaer and Brinell show that the cost of the electrolytic iron would be from 2½ to 3 cents per pound (453 g.), depending upon the cost of power, though the inventor claims that the cost is below 2 cents.

In 1911 Fischer took out patents[6] for the manufacture of ductile electrolytic iron in which he claims that ductile iron may be deposited from a hot solution of ferrous chloride if hygroscopic salts, such as the chlorides of calcium, magnesium, or aluminum, are added to the electrolyte. He claims that the ductility of the product increases with the electrolyzing temperatures and that perfectly ductile iron is obtained at temperatures varying between 100° and 120° C. The preferred solution consists of a highly concentrated mixture of ferrous and calcium chlorides, 450 parts of ferrous chloride, and 500 parts of calcium chloride being dissolved in 700 parts of water. Under these conditions a current density of 180 amperes per square foot (20 amp. per sq. dm.) may be used.

Fischer's method for the production of ductile electrolytic iron is used by the Langbein-Pfanhauser-Werke of Germany for the commercial production of sheets and other articles. Duisberg[7] states that by this method the iron is deposited free of hydrogen and that its hardness sinks below that of silver and gold, and is not much greater than aluminum.

Ramage[8] took out a patent in 1911 in which he makes electrolytic iron from iron ore. The ferric ore is dissolved in sulphuric acid and reduced to the ferrous state by sulphur dioxide. The anode compartment of the electrolytic cell is separated from the cathode compartment by a diaphragm. The portion of the electrolyte in the anode compartment is kept saturated with the sul-

phur dioxide which acts as a depolarizer. The electrolyte in the cathode compartment must be kept free of sulphur dioxide as the nascent hydrogen at the cathode would reduce it, depositing sulphur and contaminating the iron.

Part of the sulphur dioxide is oxidized to sulphuric acid at the anode. Ramage proposes to concentrate this liquor and distill off the acid. In this manner the products are both sulphuric acid and electrolytic iron.

In a later patent Ramage[9] dissolves iron in a ferric liquor and electrolyzes the resulting ferrous liquor in a cell with a diaphragm and insoluble anode. The ferric liquor and free acids which result at the anode are again reduced and neutralized by the impure iron to be refined. This later operation is carried out in a separate tank and the resulting liquor filtered to keep the liquor clear in the refining tank.

In 1913 Boucher[10] received a patent in which the electrolyte is a solution of one or more ferrous salts, such as the sulphate or chloride. This is stirred in contact with the air before electrolysis to form iron-oxychloride which reacts with the hydrogen formed at the cathode and therefore acts as a depolarizer. The electrolyte is described as having a clear chestnut brown color and should not foam. During electrolysis, oxidation may be controlled by means of an adjustable opening in the cell cover. To reduce any ferric salts formed the electrolyte is passed over iron shavings in a separate vessel at a speed varying with the current density and with the amount of phosphorus in the cast iron anode. If this amount is one percent, a circulation of four liters per hour per ampere is suitable. The concentration of the electrolyte is regulated in accordance with the amount of air supplied, but must be maintained constant during working; a suitable density is 35° to 40° Bé. The cathode is rotated at a speed proportional to the current density; peripheral velocities of 100 to 120 meters per minute are suitable respectively for densities of 45 to 72 amperes per square foot (5 to 8 amp. per sq. dm.). The temperature of the electrolyte is raised for high current densities but must not vary during electrolysis; it may be 50° and 75 to 77°C., respectively, for densities of 36 and 90 amperes per square foot (4 and 10 amp. per sq. dm.). Iron thus obtained is annealed and is then ready for commercial use.

Reed's patent[11] covers both the manufacture of electrolyte iron and the making of sulphuric acid as a by-product. The electrolyte is a solution of iron sulphate. The anode is made of spongy lead which becomes sulphated as the electrolysis proceeds. By this method free sulphuric acid does not form in the electrolyte and there is no tendency for the cathode to dissolve. The resulting lead sulphate is treated electrolytically in a separate receptacle and the sulphuric acid recovered. It is claimed that the electrolytic iron is free of hydrogen.

In 1913 Cowper-Coles[12] obtained a British patent in which he proposes to avoid exfoliation and brittleness in electro-deposited iron by suspending an iron sponge in an electrolyte used for refining iron. He claims to make iron tubes, ingots, sheets or produces pure iron directly from ores. The electrolyte is a concentrated solution of $FeSO_4$ or $FeCl_2$ which is electrolyzed, with or without a rotating cathode. As an example he states that a nearly boiling solution containing 1500 grams $FeSO_4$ per liter is used as electrolyte and under such conditions the current density may be as high as 40 amperes per square foot (4.5 amp. per sq. dm.). The iron sponge may be gotten by roasting a sulphide or other iron ore, with recovery of the sulphur and then reducing by gas.

Guillet,[13] in a paper before the Iron and Steel Institute in 1914, described the process of the French Company "Le Fer" at Grenoble for making electrolytic iron. This company makes tubes, sheets, and material to be melted, the raw material being pig iron. A cathode revolving in a neutral solution of iron salts is used, the solution being maintained neutral by the circulation of the electrolyte over the surface of the iron. The bath also receives periodic additions of a depolarizing medium such as the oxide of iron. About 90 amperes per square foot (10 amp. per sq. dm.) is the current density used.

An iron having the following average analysis is claimed to be produced after removing the gases:

	Percent.
Carbon	0.004
Silicon	0.007
Sulphur	0.006
Phosphorus	0.008

Guillet states that it is possible to guarantee phosphorus lower than 0.010 percent. When a current density of 90 amperes per square foot (10 amp. per sq. dm.) is used the yield per kilowatt year is two tons of metal, including cost of power for accessory service. The iron is annealed at 900°C. after which it possesses a high degree of ductility and can be readily worked. The current density used would depend upon the cost of power. By using a current density of 45 amperes per square foot (5 amp. per sq. dm.) instead of 90, four tons of iron may be produced per kilowatt-year instead of two as the voltage drops one-half. Where the cost of power is high the current density should be low to secure higher efficiency. Guillet estimates that the total cost would be from $30 to $40 per ton in France according to locality. The cost in the United States would probably be near $50 owing to higher cost of power, labor and materials.

The process described by Guillet is similar to that described by Cowper-Coles.[2]

The various processes described for the production of electrolytic iron vary from the simple one used by Burgess to the complicated process of Boucher. While the more complicated methods use the cheaper pig-iron and iron ore as sources of raw material, it is doubtful whether the cost of the finished iron is much less than in the simple refining process. The cost of rotating cathodes, removing slimes, solution maintenance, auxiliary apparatus, and the necessity of careful chemical regulation of the electrolyte minimize the advantage of low cost of raw material.

USES FOR ELECTROLYTIC IRON.

Electrolytic iron when deposited by the usual methods is brittle, due to the hydrogen present. In this form it can be easily broken into small pieces and even ground into a powder. By heating the iron to a red heat the hydrogen is driven off and the iron becomes ductile, the ductility increasing with the temperature of annealing.

Brittle electrolytic iron as deposited is highly soluble in acids,[14] being much more readily soluble than zinc. Annealing the iron makes it become more resistant to acid attack than ordinary irons and steels. This property of the brittle iron has resulted in the suggestion that it be used for the manufacture of hydrogen by acid attack in place of zinc and other forms of iron.

The brittleness of the iron and its purity make it an ideal material for melting in crucibles, the hydrogen content having the additional virtue of forming a reducing atmosphere. The brittleness also allows it to be readily broken into small pieces for introduction into the crucible.

The high purity of the iron makes it possible for it to be used in competition with Swedish iron and at approximately the same cost.

It may also be used for pharmaceutical purposes as a base for compounds of which iron is a constituent. Here again its purity is of value.

The much suggested use of electro-deposited iron for electromagnetic purposes appears to be becoming of commercial importance. While the magnetic qualities of electrolytic iron seem to be superior to the commercial silicon irons its high electrical conductivity counteracts this favorable property.

Electrolytic iron also is used as a basis for scientific experimental work on the various properties of iron where the purest available iron is needed to secure the most accurate data. It is also used as a basis for "pure iron" alloys.

The materials that have been produced and which seem to give the most promise for direct production without further mechanical working are sheets and tubes. By producing these directly by deposition in such a manner as to not require further operations it would be possible to make thin sheets and tubes of great uniformity. In tubes having thin walls made by mechanical processes, these often vary in thickness and it is hoped that this defect will be overcome by making them electrolytically.

EFFECT OF ADDITION AGENTS UPON THE DEPOSITION OF IRON.

The effect of addition agents upon the electro-deposition of iron has been studied by Watts and Li.[15] The solution used for experimental work contained 150 grams of $FeSO_4.7H_2O$, 75 grams $FeCl_2.4H_2O$ and 120 grams $(NH_4)_2SO_4$ per liter with a specific gravity of 1.125 at 20° C.

The addition agents giving the best results are given in the following table in order of excellence (amount given is per liter):

a. 6.0 grams ammonium oxalate.

b. 0.6 gram formin or hexamethylenetetramine.

c. 2 drops phenol.
d. 4 drops formalin.
e. original solution.

These results show that the deposition of electrolytic iron may be improved by addition agents.

DETAILED ESTIMATE ON COST OF ELECTROLYTIC IRON.

The appended data covering in detail the cost of producing electrolytic iron on a large scale has been kindly furnished by Mr. C. F. Burgess. The plant is assumed to be 1000 kilowatt capacity with an output of 8640 tons per year of 360 days.

A current density of 10 amperes per square foot (1.1 amp. per sq. dm.) is assumed and an energy consumption of one kilowatt hour for every two pounds of iron is also taken as warranted by past experimental work.

The most suitable anode material would probably be the crop ends of very mild steel, preferably the product of a basic open-hearth furnace, or even better from concerns which are making the newer higher purity irons. These materials would have the advantages of low phosphorus and manganese and also of the other elements, which should have the least tendency towards sliming and consequent deterioration of the electrolyte.

It probably could be purchased at an average of $15 per ton and would be worth $20 per ton rolled into a form needed for use in the refining tanks. This figure would cover also the freight charges to the plant.

The estimate of Table II shows a total investment of $128,360. This does not cover the total capital required. It does not include, for example, real estate investment other than that involved in $1 per square foot (0.1 sq. m.) of building space; it does not provide for working capital or accumulated stock, nor does it provide for development work which would be necessary.

Table III gives the principal items of operating cost, which show that a figure of about $10 per ton of refined iron is possible. In fact, this is believed to be a liberal estimate. It is larger than the figures given for the refining of copper, and in all probability the cost of refining iron would not be materially greater than that of refining copper. The operating costs, however, do not include interest on investment.

The cost of raw material is taken at $20 per ton, thus making the cost of the electrolytic iron approximately $30. If it would become necessary to use a low phosphorus rolled stock worth $30 a ton the cost would be increased 33⅓ percent, which would limit the use of the refined iron.

APPENDIX.

Table I.

Estimate on Electrolytic Iron Plant.

Power consumed in tanks.....1000 kw.
Output, refined iron.....24 tons per day (8640 tons per 360 days)
Refining Tanks—
- Made of 2 inch (5 cm.) cypress lumber, re-enforced.
- Size, 6 ft. 6 in. (200 cm.) long; 3 ft. 6 in. (105 cm) deep; 3 ft. 8 in. (110 cm.) wide, outside.
- Number, 840.
- Floor space per tank, 50 sq. ft.
- Total floor space, tank room, 42,000 sq. ft.
- Cost of each tank—
  - Lumber, 190 ft., at 5 cents..... $9.50
  - Labor and re-enforcement..... 9.50
  - Fittings, drains, pipings, and conductors..... 11.00

  $30.00

Amount of iron in each tank—
- 11 anodes 3 ft. (90 cm.) x 2 ft. (60 cm.) x 1 in. (2.5 cm.) thick =.....2530 lb. (1150 kg.) per tank
- 10 thin sheet cathodes..... 70 lb. (32 kg.) per tank

2600 lb. (1182 kg.) per tank

2600 lb. at 1 cent = $26.00.
Electrolyte, at 33 cents per cu. ft. = $23.00.

Table II.

Cost of Electrolytic Installation.

840 tanks, with fittings, at $30.....$ 25,200.00
Electrolyte 840 x $23..... 19,320.00
Iron under treatment—
- 840 x 2,600 lbs. = 1,092 tons at $20..... 21,840.00

Total cost of tanks $66,360.00
Cell room—42,000 sq. ft. (3,800 sq. m.) floor space.....$ 42,000.00
Additional equipment—
- Traveling cranes, pumps, storage tanks, purifying tanks, etc. 20,000.00

Total investment inside switchboard.....$128,360.00

Table III.

Operating Costs.

Power, delivered to cells, 1,000 kw. at $50		$50,000.00
Engineering and superintendence		7,000.00
Labor, 20 men at $800 per annum		16,000.00
Depreciation—		
Tanks and fittings: 15% on $25,200	$3,780.00	
Electrolyte: 10% on $19,320	1,932.00	
Iron under treatment: none.		
Building: 5% on $42,000	2,100.00	
Accessories: 10% on $20,000	2,000.00	
		9,812.00
Miscellaneous repairs, etc		10,000.00
		$92,812.00

Total cost of 8,640 tons = $92,812.00
" " per ton = $10.75

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C. F. Burgess Laboratories,
Madison, Wisconsin,
February 28, 1916.

DISCUSSION.

PRESIDENT ADDICKS: Electrolytic refining processes must rely largely on the increased value of the very pure product in order to be a commercial success, and iron seems to be a metal on which we have made no impression at all. Iron is used practically altogether as an alloy, but even as an alloy it is very impure, and we seem to have made our demands on the basis of what such iron will give us rather than what a pure product would do. We have just begun to look into rail failures and similar matters, in order to determine the effect which small impurities may have.

I do not need to say that there is no immediate future for electrolytic iron, but there seems to be a field for investigation, and, possibly for some electrolytic processes for handling iron itself from the ore.

JOSEPH W. RICHARDS: I would ask some of our Pittsburgh friends whether it is true that a plant near Pittsburgh is producing electrolytic iron from its waste pickling liquors?

F. C. MATHERS (*Communicated*): The use of ammonium oxalate as an addition agent in the deposition of iron is of special interest to me, in that it seems similar to the use of tartaric acid

in the deposition of silver. I would like to know the rate at which the ammonium oxalate is used up, what effect a large excess of it (50 to 100 gm. per liter) has upon the deposit and whether or not it increases the carbon in the deposit.

O. W. Storey (*Communicated*): As there has not been enough experimental work done, and that which has been done is not available, I cannot answer Mr. Mather's question.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

SOME UNSOLVED PROBLEMS OF THE ELECTRO-PLATER.

By George B. Hogaboom.

Dr. Watts, in recently addressing an assemblage of electro-platers, remarked: [1] "When information on such matters as these is available to those interested, your friends—the electro-chemists—will no longer spend months or even years in perfecting deposition from some particular electrolyte that could never be used in competition with present solutions on account of too great cost. Platers suffer no inconsiderable loss because of misdirected effort on the part of electro-chemists, who, from a lack of published information on the relative cost of the different operations necessary to plating, devote much of their time available for experiments in plating, to maters of trifling importance, or even entirely useless. I speak with some authority in this matter from sad experience." Those remarks are to the point and emphasize that what is needed is whole-hearted co-operation and wholesome criticism for that alone will bring the electro-plater and the electro-chemist together.

The evolution of electro-plating solutions seems to have been divided into three distinct cycles—the complicated, the extremely simple, and the efficient. In the early days of the industry the construction of a solution was very complicated and little attention was given to the amount of metal deposited in a given time, or to either anode or cathode efficiency.

About five years ago, with the advent of rapid plating salts, the pendulum, like in so many other cases, swung to the other extreme, and the simple solution, one with a cyanide of the metal and an alkali cyanide, or, in the case of nickel deposition, a single nickel salt solution, was considered the only way to get a fast deposit; the speed mania had taken hold of the plating fraternity.

At the present time the pendulum is beginning to approach a

[1] Monthly Review, American Electro-Platers' Society, January, 1916.

more rational swing. The simple solution did not live up to its reputation, but it did do one thing, and that was to set the electro-plater to thinking. It was evident that the day of the complicated solution had passed—it was not efficient; the simple solution lacked some of the good qualities of the complicated one and now, at the present time, the electro-plater is entering into the third cycle and his quest is for an efficient electro-plating bath. How to obtain that is the one great unsolved problem and in its solution the services of "his friends—the electro-chemists" are of inestimable value, but they must have unreserved assistance from the electro-plater. They are "useless each without the other."

In collecting data for this paper 250 letters were sent to as many foreman platers, publicity was given in two periodicals,[2] yet a discouragingly small number of answers were received. Not that there are no unsolved problems, but because the electro-plater has so far failed to realize the importance of electro-chemical research work. Some of the answers received were only problems of the individual—those of trying to duplicate some finish or overcome some local difficulty.

There is one way in which much assistance could be given the electro-plater aside from research work, and that is in giving him standardized electro-plating chemicals and general supplies.

While standardization is needed and some very valuable work is being done by the U. S. Bureau of Standards[3] on electro-typing solutions, under the direction of Dr. William Blum, nothing of a definite nature can be done with electro-plating solutions until they are studied in the same manner. The construction of the solutions that are now being used commercially must be known and also the value of the metallic and chemical salts, and the effect of the several addition agents.

A member of this society who is one of the foremost men in his line of electro-plating, submitted the following problems, which illustrate those of one branch of the industry:

1. To what extent is the nature of the electro-deposit influenced by the physical structure of the metallic base, such as steel, copper, brass, britannia, german silver, etc.?

[2] Metal Industry, December, 1915.
Monthly Review, February, 1916, American Electro-Platers' Society.
[3] Circular No. 52, U. S. Bureau of Standards.

2. What is the best cleansing process to use on buffed german silver flatware, to produce 100 percent perfect plating?

3. *Ditto* on steel and hollow-handle table cutlery?

4. What is the best method of obtaining a smooth adherent silver deposit upon perfectly cleansed german silver flatware?

(*a*) By placing directly in silver strike?

(*b*) By use of mercury dip followed by silver strike?

(*c*) Striking in nickel bath followed by silver strike?

5. What is the best method of obtaining smooth adherent silver deposit upon steel and hollow-handle table cutlery? Is it best to strike the silver on direct, or place in nickel bath and strike with silver afterward?

6. What composition of silver bath will produce the most efficient deposit, *viz.,* most smooth and rapid, upon german silver flatware, hollow ware, deposit work, table cutlery?

What is the highest current density that can be used in this bath to obtain smooth deposits at 65° F. (18° C.) and what agitation is best?

7. What simple, rapid and convenient method is there for determining the amount of nickel and free acid in the nickel bath?

8. What simple method is there for determining the cause of nickel solutions working dark or otherwise unsatisfactory? What is the remedy?

9. How can the rusting of silver-plated table cutlery, while in use, be prevented?

10. What causes silverware to "spot out" before it reaches the consumer?

Problem 1 is most interesting in that it opens up a field of thought to which very little attention has been paid. We know of some work that has been done along that line which has proved beyond doubt that the character of the deposit is materially affected by the structure of the metal receiving the deposit. Especially is this true of steel and German silver.

In problem 7 a question is asked which the electro-chemist on first thought would answer by saying that it would be a simple matter to titrate a nickel-plating solution for the free acid present. We know of no indicator that will give a good end point in the

volumetric determination of the free sulphuric acid using a regular standard soda solution for titration if organic acids are present. Of all the books upon electro-plating which give the method of analysis for nickel-plating solutions, Langbein alone speaks of the estimation of the free sulphuric acid,[4] in the presence of organic acids.

In the bath recommended by Mathers,[5] Stuart and Sturdevant both boric acid and ammonium citrate are used in a solution containing both nickel sulphate and nickel ammonium sulphate. If the bath is to be kept constant in metal and free acid how shall the plater proceed to analyze it?

Problem 10 not only applies to silver-plated articles but also to brass, copper and bronze-plated objects.[6] Much work has been done in trying to solve the "spotting out" problem but it is still with us. We have seen work baked out, boiled out, given alternate dips in hot and cold water to remove the occluded salts, neutralizing solutions used, plating in cyanide of potassium instead of cyanide of sodium and *vice versa,* and, at times felt confident of success only to find on the following day the same attack of "measles" even under the protective coating of lacquer.

The pitting of nickel deposits is another problem to which the electro-plater has given much thought without being able to find a remedy. We disagree entirely with Mathers, Stuart and Sturdevant that pitting is caused "by the adherence of loosened insoluble particles of anode or other hard material." . . .and that "The buffing pulls these adhering particles away, leaving holes in the nickel." Such holes have never before been considered as "pitting," and the authors fail to distinguish between a rough and a pitted deposit. Pitting occurs upon smooth adherent deposits that color up easily on the buff, and there is no evidence of "holes" in the deposit. It may and very probably is caused by the adherence of gas bubbles, and, contrary to the same authors has, in a measure, been prevented by agitating the solution with air or keeping the cathode in motion. If a bath is agitated, however, the sludge will cause rough deposits and unless pure nickel anodes are used iron, with which nickel anodes are alloyed, will be deposited with the nickel. If a small enough current or volt-

[4] Electro-deposition of Metals, Langbein, 5th edition, pp. 309-310.
[5] Transactions American Electrochemical Society, 29, 8 (1916).
[6] See various articles in Brass World and The Metal Industry.

age was used the efficiency of the bath would be greatly decreased and another exception, pitting, occurs more often in baths slightly acid than in those which are almost neutral.

Bennett,[7] Kenny and Dugliss, in their experiments with nickel solutions, found that "The best deposits are obtained when the solution is alkaline at the surface of the cathode" and "The efficiency is dependent upon the degree of alkalinity of the cathode film." It is too bad that the subject of "pitting" was not thought of in those experiments, for we believe that the cause would have been determined. It is probable that "pitting" is caused by the primary deposition of hydrogen at the cathode and, if there was an alkaline film at the cathode, that would be prevented and the nickel be deposited primarily instead. In that case there would be no gas bubbles on the cathode and consequently no "pitting."

Other problems submitted were:

11. How can nickel deposits be made to adhere firmly to tin or tinned articles?

There is no difficulty in depositing nickel upon tin so that it will stand buffing, but if the deposit becomes broken it can be peeled off in strips very easily. The condition is true of imported nickel-plated tinware as well as domestic.

12. What are the factors controlling the hardness or stiffness of copper deposit? It is well known that this is dependent upon the rate of deposit, amount of free acid in the bath, temperature, impurities, etc. Why is the deposit hard or soft? The hardness is not essentially accompanied by either fine- or coarse-grained deposits. The problem is to get a hard deposit independently of the rate of deposit and at will.

13. A practical solution for the deposition of chromium is greatly desired. Chromium deposits are less susceptible to the action of the air and moisture than nickel and therefore tarnish less easily.

14. A positive rust-proof coating, black in color, for iron and steel, without the use of excessive heat.

15. A dip to produce a brass coating on iron and steel by simple immersion, similar to a copper dip.

[7] Bennett: Transactions American Electrochemical Society, 25, 335 (1914).

16. Why will a single nickel salt solution plate zebra-like black and white streaks when the work is given a mechanical motion during the deposition while it plates very satisfactory, white and smooth, when used as a "still" solution?

17. A substitute for platinum chloride to produce the same color effect upon silver. Platinum black is the only durable and satisfactory color for "oxidized" and "French gray" finishes at the present time.

18. Arsenious acid added to a cyanide brass solution brightens the deposit. It also materially decreases the efficiency of the bath. It is well known that the presence of arsenic in copper wire injures its conductivity. Does it affect the deposition of copper from a brass solution in the same manner?

19. If a cyanide copper solution is made from an alkali cyanide, cyanide of copper and a small amount of soda ash, the anode efficiency cannot be maintained at 100 percent unless the free cyanide content is kept at such a point that a slight decrease in the metal content will cause blistering of the deposit. What salt can be added that will corrode the anode, producing a compound that will be easily soluble in the free cyanide, and thereby keep the anode clear? Bisulphite of soda is recommended by Roseleur,[8] Langbein,[9] Barclay[10] and Hainsworth and other writers on electro-plating. That salt decomposes the free cyanide and decreases the cathode efficiency. Large amounts will result in only a slight film of copper being deposited. Watts[11] recommends bi-tartrate of potassium, which is very expensive and would increase the cost of production. Miller[12] advises aqua ammonia, the effect of which is soon lost in a hot solution.

20. A successful cyanide of zinc solution, one in which there would be a fairly good anode corrosion so that the bath could be kept uniform in metal content.

21. A plating rack or a covering for one that would not be coated with metal except at the points of contact with the articles to be electro-plated. Tons upon tons of metal are deposited upon

[8] Galvano-plastic Manipulations, Roseleur, Fesquest translation, 1872, p. 88.
[9] Electro-deposition of Metals, Langbein, 5th Edition, p. 321.
[10] Electro-deposition of Metals, Barclay and Hainsworth.
[11] Transactions Am. Electrochemical Society, **27**, 141 (1915).
[12] Transactions Am. Electrochemical Society, **26**, 63 (1914).

racks every year which must be refined at a heavy expense or be sold as scrap metal.

22. A satisfactory solution for the deposition of a true bronze, *i.e.*, copper and tin. Fields[13] recommends a double ammonium oxalate solution. In experimenting with this solution Mathers found that at "first such a bath gives a rough copper, then a bright copper and then a bronze which gradually becomes whiter until it is as white as tin." He was unable to maintain conditions required for a rich uniform bronze.

23. A brass solution from which the metal can be deposited as efficiently as copper can be from an alkali cyanide bath and not be coarse or brittle. One in which the anode efficiency will approximate 100 percent without the addition of large amounts of aqua ammonia or any ammonium salts which either quickly decompose or decrease the cathode efficiency.

24. What is the comparative value of cyanide of potassium and cyanide of sodium in relation to the corrosion of the anode, solubility of the compound formed at the anode, and conductivity, in the commercial electro-plating solutions generally used?

In conclusion I wish to thank those who assisted me in trying to catalogue some of the unsolved problems of the electro-plater.

DISCUSSION.

G. B. Hogaboom: I am glad that I have been able to present some unsolved problems of the electroplater. There are many. The plating field is a virgin field. While the beginning of electrochemistry was electroplating, still there is very little known about it, and in presenting these problems I have tried to get the views of nearly all of the most progressive electroplaters, members of the American Electroplaters' Society, an organization which is based entirely upon educational features for the development of the industry.

President Addicks: I think this is a splendid paper. I hope we are not going to allow these six or eight pages of questions

[13] Principles of Electro-deposition, Fields, p. 253.

to be thrown at us, and let them go without giving anything in return. I will take up two or three of them myself.

Questions 10 and 16 deal with "spotting out." It seems to me that there may be some photo-chemical effect, as the haloid salts are sensitive to light, particularly those of silver and copper, but we are dealing with solutions, especially in the case of nickel plating, which have chlorides present. In the work I have done in plating copper out of copper solutions, where chlorine was present, some cuprous chloride comes down at the cathode; the cathode looks normal in the solution, but by putting it in the sun with anything placed over it, it will take a print of the object in a few minutes. The fact that "spotting out" occurs under a lacquer which would be translucent to light is very suggestive, and it may be that it is the presence of chloride in the solution that does it.

In the cyanide solution these chlorides would be in solution, but when you wash such a cathode some of the chloride may be precipitated and show nothing at the time, but the next day all of this blackening appears.

Question 12 raises the point of how to get hard copper. That is a place for the addition agents to be investigated. We know that the ordinary copper cathode in a pure solution is soft metal, whereas when glue is added it becomes very hard.

Question 21 refers to the problem of getting a cathode hook that will not be plated on. There is a suggestion, which I suppose has been tried and rejected, which I would make in this connection, and that is to use ordinary insulated wire with only a little place scraped off for the contact.

William Blum: Reference has been made to the work of the Bureau of Standards on Electroplating. I was glad to hear that the work we are doing in a limited field in electro-deposition has been of value to the related industries. Incidentally I may point out that while this work has been done on perhaps the simplest plating bath, the copper sulphate sulphuric acid bath, from it we may be able to learn some general principles which will be of assistance in work which we hope to do later upon other phases of electro-deposition.

This work, while it has been reported on briefly to technical

societies, especially to electrotypers, has not been sufficiently completed to render a full report such as we would desire to make to this Society. We have on hand in the south building some of the specimens and results obtained in this work on the deposition of copper which we will be glad to have you see, and which we will explain to anybody especially interested in that line of work.

Regarding question 12 in Mr. Hogaboom's paper, as to the factors affecting the hardness or stiffness of the copper deposits, we found in a regular copper sulphate bath, working within a limited range of temperature, about 25° C. to 40° C., that the temperature had a greater influence than any other single factor. This difference of only 15° C. in temperature would frequently make a difference of more than 100 percent in the tensile strength of the deposited copper. Invariably it was found that copper deposited at 40° C. had a much lower tensile strength than that deposited at 25° C. I will not attempt to go into the details of these observations at this time.

As to colloids, to which reference was made, while we have made no actual study of baths containing colloids. we have, for the purpose of comparison, tested copper deposited from such solutions. We find that while the hardness and tensile strength of such copper is high, the ductility (as measured by the elongation), is verv low. Thus we may have copper deposited from the regular acid sulphate bath with a tensile strength from 14 to 28 kg. per sq. mm. (20,000 to 40,000 lb. per sq. inch.) and from 20 to 30 percent elongation. On the other hand copper deposited from baths containing colloids may have a tensile strength as high as 35 kg. per. sq. mm. (50,000 lb. per sq. in.) and an elongation of only 5 percent. While there may be cases where hardness is the main requirement, it will usually be gained at the expense of ductility.

F. C. Mathers (*Communicated*): The criticism of statements made by the writer of this discussion concerning "pitting" of nickel deposits is merely a misunderstanding of the definition of the word "pitting." In the statements referred to, the authors designated as pitting all depressions or holes in the nickel plate. They are glad to know the distinction between those caused by gas and those caused by the pulling away of solid loosely attached particles from the cathode during buffing.

Problem 8. Excess of sodium, potassium or ammonium salts cause darkening of the deposits. The effect is greater with ferro-nickel than with pure nickel anodes. The addition of double salt to a bath introduces an excess of ammonium sulphate.

Problem 10. Is there any silver bath or any condition of operation known that is *sure* to produce a deposit that "spots out?" This information would help anyone who wished to work on this problem.

CARL DITTMAR: Referring to Question No. 20, as to a successful alkaline zinc solution, it seems strange that while Mr. Hogaboom was propounding the alkaline solution as an unsolved problem, we have been doing some experimental work in exactly that direction, and I have several samples with me which I want to show, but unfortunately cannot give very much data regarding them, as some of the samples were finished as recently as two days ago, and I think, before giving out any data as to the preparation and operation of the solution, we would rather see whether the solution is quite as ideal as we think it is.

J. C. ANDREWS: The use of sodium alizarin sulphonate as an indicator in the control of alkalinity or acidity of nickel plating solutions might be suggested as an aid towards the solution of problem No. 7.

It has been proven that the efficiency of a nickel bath may be increased by the proper control of the amount of alkalinity present. To control the alkalinity in commercial operation of plating solutions presented some difficulty until an indicator was found which acted more uniformly than the regular indicators we find in general use, namely litmus, congo red, and methyl orange.

H. E. PATTEN: In regard to the approach to a neutral point in brass plating solutions, I will ask Dr. Blum if he has applied to his electroplating work the considerations which he has already published in connection with the use of the hydrogen electrode.

I will elaborate a little. In using an organic dye, either acid or basic in its nature, as an indicator of the approach to neutrality, we are met with the situation that a dye changes its color at a certain so-called free acidity, or hydrogen ion concentration. It would be perfectly natural to conclude that with different organic

salts, each having its own characteristic as to free acidity, that they would not all give a satisfactory neutral point. It is possible that Dr. Blum has that in mind in his work, and might have applied it.

We are working along the same line in determining the free acid of fruit juices. The biologist uses this same method in getting the death points in bacteria, etc. We find there is no such thing as a perfectly definite neutral point, and you have to define what the solution is neutral to.

WILLIAM BLUM: Thus far our study of nickel solutions has been confined to a few observations, as we have had no opportunities for investigating them in detail. We have in mind, however, the application of the hydrogen electrode to the study of nickel solutions, as being promising, and perhaps throwing light on the small factors which may have very great effects in the deposition of nickel. It is possible to titrate and get at least relative results, using methyl orange to indicate the end point, by comparison with a neutral nickel solution. The results are certainly more accurate than those obtained with litmus paper. We have found that a difference of less than 0.1 g. per liter (of free ammonia) in the alkalinity of a nickel solution made in some cases a difference of 2 percent in the iron content of the deposited nickel. Since there is a critical point of neutrality where iron in the solution will be all precipitated as iron hydroxide, it is evident that the iron content of the deposited nickel is dependent, not so much upon the composition of the anode as upon the neutrality of the solution. While we cannot throw any light on the best method for determining the acidity of nickel solutions containing weak acids, we can at least emphasize the importance of such determination.

PRESIDENT ADDICKS: A reagent some of the copper refiners use as an acid indicator where they have mixed sulphates of iron, copper and nickel, is dimethylamidoazobenzol in saturated alcoholic solution.

F. C. FRARY: In regard to the spotting on the silver, while there has been some controversy over the matter, it seems to be clearly established that in the electro-analytical determination of silver from cyanide solutions which do not contain a considerable

excess of cyanide, there is always an occlusion of cyanide in the silver. We tried it some years ago and were able to obtain good tests for cyanide from silver deposited out of cyanide solution, even after boiling the silver with water.

Has anyone tried to correlate the "spotting out" problem with occasions when the excess of free cyanide in the bath was lower than usual, which might establish a favorable condition for the occlusion of cyanide?

G. B. Hogaboom: I wrote a paper upon that subject, and it was published in "The Metal Industry" some two or three years ago. I thought I had solved the problem of spotting out. It was on heavy silver deposit work which would run for twenty-four hours, and we put on 0.023 inch, on glass, and in that case the "spotting out" was eliminated by a low free cyanide content. But recently I have had some work on steel knives, where the metal content has been 3 oz. per gallon (318 g. per l.). The free cyanide content has been ½ oz. per gallon (53 g. per l.), and there has been more "spotting out" than when we used an equal amount of cyanide and metal, like 3 oz. (85 g.) of metal and 3 oz. of cyanide, and it has knocked the props from under my argument entirely. The spotting seems to occur just the same.

In regard to the lacquer of which Chairman Addicks spoke, spotting out occurs on unlacquered materials, just the same.

President Addicks: I was trying to explain the photo-chemical action, showing the atmosphere played no part in it. It will occur either with lacquer or without lacquer. The photo-chemical action is quite strong in casting silver bars, where salammoniac is used as a flux.

H. J. Blanchard: In connection with the silver plating of steel knives, I would ask Mr. Hogaboom if he thinks the purity of the steel has anything to do with the nature of the deposit. We are having troubles in electroplating steel knives, which we did not have when we could get the quality of steel we wanted. I wondered if the purity of the steel had anything to do with the matter?

G. B. Hogaboom: The structure of the steel directly affects the character of the deposit. When it is coarse due to not receiving

the proper heat treatment, the surface, while it may be highly glazed, will not be as clear after plating and burnishing as it would have been had the crystals been smaller. Low carbon steels do not plate as well as those of higher carbon content and alloy steels are still better, if given the proper annealing and hardening treatment.

WALTER ARTHUR: I think there is a point which could be taken up as a matter of value to the electroplater. Perhaps it is a point we have been overlooking. Some years ago I had occasion to rather extensively examine micrographically the different kinds of galvanized iron, and I found in every instance of sherardized iron, cold galvanized and hot galvanized, there was an alloy formed between the zinc and the iron. I examined other plated metals and found the same. It is possible that the crystalline structure of the metal has a great deal to do with the kind of alloy that is formed between the metals. I think considerable light might be thrown on the subject if the platers will take occasion to make sections through these knives that have been spoken of and examine the nature of the alloy underlying the silver. They may find in a number of cases that the alloys are too thin, or too weak, to hold the silver on to the iron. I think perhaps this thing has not been given sufficient attention, and a study from this standpoint might yield valuable results.

G. B. HOGABOOM: It is not the peeling off that is the point, it is the deposit that reflects the structure of the metal under the plating. The gentleman is correct in his assumption that a study of the subject from a metallurgical standpoint would be advisable, and some work has been done along that line, but only upon cold-rolled stock, and not upon forged steel.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

NICKEL PLATING.

By F. C. Mathers, E. H. Stuart and E. G. Sturdevant.

This work was undertaken at the suggestion of Dr. W. D. Bancroft, chairman of the Committee upon Electroplating appointed by the American Electrochemical Society in May, 1913. The idea in this work was to find the nickel plating bath which would give the best deposit at the highest current or voltage, and to discover the effect of each constituent of the bath on the plating operation.

It is not assumed that the results obtained in the laboratory with small baths can be duplicated exactly in commercial work, but it is thought that these results may point the way to improvements in nickel plating. The man who works daily for long periods of time at nickel plating finds out many things about the solutions that never occur to one engaged in the scientific study of a bath for a short time. The practical plater must make the final decision concerning the best bath.

Unfortunately there was no method of quantitatively recording the value of the deposits from the various baths as regards smoothness, adherence and softness, consequently the deposits can only be qualitatively compared by a word description of their general appearance and properties.

Manipulation.

Beakers of 350 cc. (0.74 pints) capacity were used as electrolysing vessels. The volume of each bath was 300 cc. (0.61 pints). Two anodes and one cathode were used in each bath. The distance between the anodes was 4.5 cm. (1.77 in.) hence the distance from the cathode to each anode was 2.25 cm. (0.885 in.). The anodes, unless otherwise stated, were the ordinary nickel-iron alloy containing about 92 percent nickel and about 6.5 percent iron. In some of the work, "strip" pieces of 99.8 percent

electrolytic nickel cathodes were used directly as anodes. These are referred to as "pure." The anodes were suspended by lead strips and were placed in cloth bags. The area of the cathode and the area of the anodes on the sides towards the cathode was each 50 sq. cm. (0.78 sq. in.). The cathodes of sheet copper were polished with tripoli and rouge on a cloth wheel and then carefully cleaned with the usual precautions. Electrolysis was at room temperature, 22° C. (72° F.). In preparing the baths, the boric acid was added after the other constituents had been dissolved in water, neutralized with nickel hydroxide or carbonate and filtered. The composition of the baths, given in percent by volume or parts in 100 parts of water, may be changed to ounces per gallon by multiplying by 1⅓, or to be more exact, 1.3361. Unless otherwise stated, a current density of 1.6 amp. per sq. dec. (14.8 amp. per sq. ft.) was used when possible, but if this high current produced a black deposit or caused gas evolution, the current was reduced until a good deposit was obtained. Electrolysis was continued for 1.25 hours, thus giving a deposit approximately 0.001 in. (0.0025 cm.) thick, which is a greater thickness than is generally produced commercially. If the bath was run at a lower current, electrolysis was continued until the deposit reached this thickness. A poor bath may give an apparently good thin deposit at a low current but only a really satisfactory bath will give a good thick deposit at this unusually high current.

Voltage readings were of little value because of variations caused by impurities in the anodes and by changes in distance between electrodes. In the better baths the voltage was about 2 to 2.3.

In the course of this work several hundred baths were prepared and tested. The first step was to make up the various baths which were described by Watts[1] in the review upon nickel plating. It was found that all of the baths which gave good deposits contained a comparatively few salts[2]. The salts most commonly used are: nickel ammonium sulphate, nickel sulphate, nickel chloride, boric acid, magnesium sulphate and sodium chloride. The less usual additions are citrates and tartrates.

[1] Trans. Am. Electrochem. Soc. (1913), 23, 99.
[2] Mr. H. V. Houseman assisted with this part of the work.

The result of changing the proportions and combinations of these salts was further investigated. It was thought necessary to report in this paper only the most important final data and conclusions, which are as follows:

Pitting.

Pitting of the cathode is caused both by the adherence of loosened, insoluble particles of anode or other solid, hard material and by the adherence of gas bubbles. Before buffing, cathodes with much of this adhering material, feel somewhat like sandpaper. The buffing pulls these adhering particles away, leaving holes in the nickel plate. This trouble can be best avoided by keeping the anodes in bags which retain all the loosened material. It can also be prevented by not stirring or agitating the solution within eight hours of the time of using, thus allowing the solid particles to remain upon the bottom. The formation of gas bubbles may be largely avoided by using a small enough current or voltage, by selecting a good composition of bath, and by maintaining the solution only slightly acid.

Use of 99.8 Percent Nickel Anodes.

Formerly a nickel-iron alloy containing about 92 percent nickel and 6 percent iron was used as anode because it was supposed that pure nickel would not dissolve. Recently there has been a tendency to use purer anodes containing at least 95 percent nickel, and not more than 2.5 percent tin, 1 percent iron and 1.5 percent other impurities. The objection to any but a pure anode is that the composition of the bath will gradually change unless all the metals dissolved from the anode are redeposited on the cathode in the same proportion in which they are present in the anode even if the cathode and anode efficiencies are 100 percent. In the ordinary plating bath part of the iron is deposited upon the cathode and part of it is oxidized by the air to a basic salt which goes into the sludge or precipitate. This produces a decrease in the concentration of nickel in the bath equivalent to the iron and nickel in the sludge, but tends to purify the deposit because only the iron remaining in solution can be deposited. Ammonium citrate in the ordinary nickel bath prevents the formation of sludge, consequently the com-

position of the bath remains almost constant but the deposit is more impure and may be darker in color because practically all of the iron that was in the anode is deposited with the nickel on the cathode. This difficulty can be avoided by the use of pure anodes made of electrolytic nickel. Some "strip stock" pieces of 99.8 percent pure nickel cathodes, kindly furnished by the International Nickel Company, were used directly as anodes. These anodes dissolved with approximately theoretical efficiency if chlorides were present in the baths. A bath containing 7 percent nickel ammonium sulphate, 7 percent nickel sulphate, 2 percent magnesium chloride, 1 percent boric acid, and 0.2 percent ammonium citrate gave an anode efficiency of 99.71 percent and a cathode efficiency of 95.67 percent at a current density of 1.5 amp. per sq. dec. (13.9 amp. per sq. ft.) at both electrodes. In a similar bath, except that magnesium chloride was absent, the anode and cathode efficiencies were 17.5 and 60 percent respectively. This shows the necessity of having some chloride present in the bath. Nickel chloride or sodium chloride was also satisfactory. In a single salt bath containing 10.5 percent nickel sulphate, 3.5 percent boric acid and 1.8 percent sodium chloride with current densities of 2.1 and 1.4 amp. per sq. dec. (19.5 and 13 amp. per sq. ft.) at both electrodes, the efficiencies were respectively 99.4 and 99.7 percent for the anodes and 98 and 98.7 for the cathodes.

There was some shedding of small loose pieces from the anodes, which made bagging necessary for the maintenance of a perfectly clear solution.

From the results of this work, it seems that pure nickel anodes should be used because of the better color of the deposit, the greater range of conditions which are possible without the appearance of dark or bad deposits, and the better maintenance of a constant composition of the bath. Pure nickel anodes are also more economical because they cost no more per pound than the 95 percent alloy.

Preventing Sludge.

Ordinary nickel baths using ferronickel anodes soon become turbid and gradually a sludge or precipitate settles to the bottom of the vessel. Very much less sludge is formed if pure electro-

lytic nickel anodes are used. Less sludge is said to be formed in single salt baths which contain no ammonium. An analysis of dried sludge from a bath using ferronickel anodes showed 39 percent iron oxide (Fe_2O_3) and 8 percent sulphate (SO_4). If the cathode reaches into this sludge, the finished plate has a frosted appearance resembling a deposit on improperly cleaned work. Deeper baths than required to hold the articles being plated must be used in order to give room for this sludge to accumulate. At intervals the entire bath must be filtered and the tank cleaned. An additional advantage of a bath free from sludge would be the possibility of moving the cathodes or stirring or agitating the solution during electrolysis whereby a greater current or voltage could be employed.

Ammonium citrate, a solvent for iron and nickel hydroxides, will entirely prevent the formation of a sludge in nickel plating baths. Only from 0.2 to 0.3 percent was required to keep the baths perfectly clear and free from turbidity during the course of the experiments tried, but further small additions might have to be made from time to time in commercial baths. Larger amounts in some baths tend to darken the deposits. In all the later experiments in this work, ammonium citrate was used, even in the single salt baths with pure anodes, because some sludge is formed in all baths which contain no citrate.

Purity and Color of Deposits.

Ordinary nickel plating should more properly be called ferronickel plating[3] because many commercial deposits contain 3 percent or more of iron in those cases where the anodes contain 6 to 8 percent of iron, which is the recognized composition of the older cast anodes. The rest of the iron goes into the sludge in the bath. The ammonium citrate, which keeps all of the iron in solution and prevents the formation of sludge, gives a deposit containing approximately as much iron as was in the anode. Using an anode containing 6.49 percent iron, the deposit contained 6.23 percent iron when ammonium citrate was in the bath but only 3.31 percent of iron in a deposit from a similar bath containing no ammonium citrate. This iron in the nickel deposit is one of the chief causes of the dark or bluish color. The addition

[3] Bancroft, Trans. Amer. Electrochem. Soc. (1906), 9, 217.

of 0.5 percent ferrous sulphate to a bath containing citrate made the deposit very much darker before buffing and more blue after buffing. Addition of another 0.5 percent of ferrous sulphate made these changes more pronounced. These cathodes were harder, less smooth and more difficult to buff. Salts of the alkali metals both organic and inorganic darken the deposits largely through their action on the iron. With pure anodes, the darkening is much less or even absent altogether.

The question of the effect of the 2.5 percent of tin which is present in the newer 95 percent anodes was not studied. The claim that these anodes produce less sludge indicates that the tin is redeposited on the cathode but the statement is also made[4] that the tin goes into the sludge as a hydrated oxide.

Lead Hooks or Wires for Hanging Anodes.

Lead hooks or wires can be used to hold the anodes in position. The entire anode can be immersed in the bath with only the lead hook extending above, consequently the scrap nickel from anodes may be reduced to almost nothing. It seems that in commercial work too, lead hooks could be used to advantage in suspending the anodes since the copper, at present used, must not touch the solution. The lead peroxidized only slightly on the surface.

Acidity and Acids.

Boric acid, 1 to 3 percent, should be used in all of the baths. Citric, acetic or benzoic acid cannot be used in place of the boric acid, perhaps due to the comparatively small quantity of these acids which can be added without making the bath acid to Congo red, but it may be that the boric acid has an action other than as an acid. With the boric acid present, the more free sulphuric acid that is added without making the bath acid to Congo red, the more shiny the deposits before buffing.

Use of Magnesium Salts and Alkaline Metal Salts.

Magnesium sulphate or chloride in baths containing nickel ammonium sulphate improves the color of the deposit by making it whiter and large amounts (up to 10 percent) can be added without any apparent injurious action even when impure anodes

[4] Sperry, Brass World, Oct., 1905.

are used. The addition of sodium, potassium or ammonium salts in rather large amounts (1 to 2 percent do not show much action) to nickel ammonium sulphate baths darkens the deposits, even when pure anodes are used, but this darkening is much less pronounced than when impure anodes are used. The less ammonium, *i. e.,* the greater the proportion of nickel sulphate to nickel ammonium sulphate the less the darkening action of these salts. In the single salt baths containing no ammonium the darkening practically ceases.

Other Salts than Sulphates.

Nickel sulphate and ammonium perchlorate in the proportion of nickel and ammonium in nickel ammonium sulphate gave deposits that were not different from those produced in nickel ammonium sulphate baths.

Nickel chloride and ammonium chloride gave deposits that were less bright than from the corresponding sulphate baths. Lead hooks as hangers for anodes were attacked in these chloride baths.

COMPOSITION OF BATHS USED.

(a). *Nickel Ammonium Sulphate or "Double Salt."*

This is the best known plating salt, but is poorly adapted for this use on account of its low solubility which limits the concentration to 8 percent for winter use and 10 percent for summer use. This bath gives a good deposit at a low current (0.3 amp. per sq. dec. or 2.8 amp. per sq. ft.) but with higher currents gas is evolved at the cathode and the deposit becomes black or pulverulent or "burned." Additions of magnesium sulphate, magnesium chloride, potassium chloride, sodium sulphate, ammonium chloride, ammonium bromide or sodium, potassium or ammonium citrates, tartrates or acetates from 1 to 8 percent decreased the current that could be used without producing the blackening or burning. When a low enough current was used to avoid the burning, the whitening action of the magnesium and the darkening action of the other salts were observed. Boric acid was the only substance which seemed to prevent the burning of the deposit at high currents. With 5 percent boric acid it was possible to get a deposit only slightly burned on the upper

edge with a current of 2 amp. per sq. dec. The addition of boric acid along with the salts mentioned above tended to overcome the blackening and allowed a higher current to be used, but not as high a current as when the salts were absent.

(b). *Nickel Sulphate and Nickel Ammonium Sulphate Bath.*

An 8 percent nickel ammonium sulphate bath contains only about 1.4 percent of nickel, a metallic content entirely too low for rapid work. With each addition of nickel sulphate to the 8 percent nickel ammonium sulphate bath, a higher current could be used without causing blackening and less boric acid was required to prevent the burning or blackening with a given current. It was found that 2 amp. produced no blackening even upon the edges if 5.3 percent nickel sulphate and 1 percent boric acid were added. With 8 percent nickel sulphate, still less boric acid (0.3 percent) was required to prevent burning. A bath containing 7 percent nickel ammonium sulphate, 7 percent nickel sulphate, 1 percent boric acid and 0.2-0.3 percent ammonium citrate was found suitable for electrolysis with the high current of 1.6 amp. per sq. dec. The effects of the various salts were then tried in this bath. An increase in the boric acid to 2 and then to 3 percent seemed not to affect the deposit except to make it more lustrous before buffing. This is, in general, the effect of increasing the acidity of the bath. Magnesium sulphate, 5, 6, and 11 percent, had no darkening action but seemed to make the deposit whiter after buffing. Sodium chloride, sodium sulphate or potassium chloride, 5, 6 and 11 percent, made the deposits increasingly darker before buffing, and more bluish after buffing. It seems that the proportion of ammonium in nickel ammonium sulphate is near the limit for pure white deposits with ferronickel anodes because a decrease in the ratio of ammonium, by adding nickel sulphate, makes the deposits brighter and makes the darkening action of the sodium less pronounced. It seems that when the sum of the sodium and the ammonium reaches a certain point in proportion to the nickel, the deposit begins to lose its pure white color. The less the ammonium in the bath, the greater the quantity of sodium required to produce the darkening. On the other hand the ammonium and the magnesium are not additive hence large

quantities of magnesium in baths containing ammonium do not produce a darkening. Ammonium shows a greater tendency to produce the darkening than does the sodium. With pure anodes the darkening action was very much less noticeable, thus showing the injurious influence of the impurity, iron. Boric acid will overcome this darkening action, but with very large quantities (15 percent) many of the deposits became covered with fine cracks. Salt which is added only on account of the better anode corrosion, due to the chloride, should be replaced by magnesium chloride which accomplishes the same results as both the sodium chloride and the magnesium sulphate without the injurious effect of the sodium.

(c). *Baths with Large Amounts of Nickel Sulphate.*

With only 4 percent nickel ammonium sulphate, 1 percent boric acid, 0.2 percent ammonium citrate and with nickel sulphate from 8 percent increasing to 16, the deposits became more and more lustrous before buffing and the darkening effect of the alkali metal salts became much less pronounced. This bath has the advantage over baths having a greater proportion of nickel ammonium sulphate, like (b), that the additions of other salts have less influence upon the color of the deposit and over single salt baths, like (d), that its slight acidity need not be so carefully maintained. This bath seemed to give the best deposits of any that was tried.

(d). *Single Salt Baths.*

Some experiments were tried with the following single salt bath which is being used commercially except for the ammonium citrate: nickel sulphate 10.5 percent, boric acid 3.7 percent, sodium chloride 1.8 percent and ammonium citrate 0.2 percent. The deposits were bright and white after buffing and sodium chloride up to 11 percent and ammonium citrate up to 3.5 percent produced only a little darkening. With pure anodes the darkening was still less.

CONCLUSIONS AND SUMMARY.

1. The purest nickel anodes obtainable should be used. Strips of electrolytic nickel cathodes, 98.8 percent pure, used directly

as anodes, dissolve irregularly and with pitting, but no impurities are introduced into the bath. Very much of the trouble with badly colored deposits and with sludge is caused by the iron from impure anodes.

2. The addition of 2 percent of magnesium or nickel chloride makes the anode corrosion approximately theoretical.

3. The nickel anodes, supported by lead hooks, may be completely immersed in the solution, thereby greatly reducing the amount of scrap metal from the anodes.

4. The anodes should be placed in bags in order to catch loosened particles which cause pitting if they reach the cathode.

5. The addition of 0.2 to 0.3 percent of ammonium citrate keeps the solution clear and free from sludge, whereby a more shallow tank and a less volume of solution may be used.

6. The bath should be stirred or mixed thoroughly at intervals but not within 8 to 10 hours of the time of using if any solid particles from the anodes are present.

7. The greater the ratio of nickel sulphate to nickel ammonium sulphate the brighter and more shiny the deposit. The more acid the solution (to the point of acidity to Congo red) the more shiny the deposits.

8. Boric acid increases the current that can be used without blackening or burning the deposit.

9. The following bath seemed to be the best: nickel ammonium sulphate 4 percent, nickel sulphate 10 to 14 percent, boric acid 1 to 3 percent, magnesium chloride 2 percent and ammonium citrate 0.2 to 0.3 percent.

10. A current density of 1.6 amp. per sq. dec. (14.8 amp. per sq. ft.) which plates a thickness of 0.0025 cm. (0.001 in.) in 1.25 hours may be used.

The authors wish to thank the American Electrochemical Society and its Committee on Assisted Research for the grant of money for the purchase of a portion of the materials used in this research.

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DISCUSSION.

G. B. Hogaboom: In this paper, on page 385, under the heading of "pitting," the following statement is made: "Pitting of the cathode is caused both by the adherence of loosened, insoluble particles of anode or other solid hard material and by the adherence of gas bubbles." I do not think that the authors of this paper have correctly interpreted the word "pitting." Pitting is never, I might say, caused by the adherence of loose and insoluble particles. I have here some samples of pitted nickel, just as they came from the bath; one has been polished, showing that pitting is a condition which is caused by the solution, and not by adherence of any particles. The adherence of particles would be called rough plating rather than pitting, and both can occur in the same solution.

The amount of metal that the authors are using is not as large as is employed in some of the most successful nickel baths. Four ounces of metallic nickel per gallon is being used in baths to get 1/1000 inch (0.025 mm.) in twenty minutes' run, and not 1¼ hours, as given by the authors; the bath contains single nickel salts, boric acid, and a chloride.

President Addicks: These samples look like chatterings from gas bubbles. What I understand by pitting is a little insoluble particle which is formed and makes an insulated spot. Then we have a nodule which stands out, and a little later that nodule will pull out, and makes a little hole.

G. B. Hogaboom: In electro-plating parlance that is not accepted. Pitting is as shown on these sample. The trouble you describe would be called holes in the metal deposit.

J. W. Richards: I looked at these samples under a magnifying glass; each one of these little pits is just as its name would indicate—a pit or depression in the surface. Most of them are spherical, some of them with a little bit of a tail to them, as if the gas bubble which caused them had attempted to rise.

Carl Hering: I might here call attention to a paper I read before this Society a number of years ago, in which, under the microscope, I showed that some of the particles which did not

form a part of the electrolyte, that is, particles suspended in the solution, traveled with the current and attached themselves to the cathode. If the electrolyte is a plating solution, metal will then be plated around these foreign particles, causing holes or producing a roughness. For this reason plating solutions should be free from suspended particles.

President Addicks: I suppose we have essentially an electrostatic field and electrostatic attraction and repulsion.

O. P. Watts (*Communicated*): This paper is a valuable addition to our knowledge of nickel plating. Information in regard to the specific effect of each of the many substances that have been used in nickel baths is of the greatest importance to progress in this useful branch of electro-plating. It is to be hoped that the evidence here presented of the harmful effects of iron in the nickel bath may be taken to heart by platers, and so hasten the day when nickel, not alloy anodes, will be universally used in the nickel tanks of the United States.

G. B. Hogaboom: Some excellent work is being done with shot nickel, using a container with a perforated celluloid diaphragm. There must be little or no ammonia salts present in the solution, or the iron that may be present will precipitate as hydroxide and insulate the shot from one another, causing poor anode efficiency.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

RAPID NICKEL PLATING.

By Oliver P. Watts.

During the greater part of the half century that nickel plating has been practiced, platers were content to follow in the footsteps of their forefathers and deposit nickel at the snail's pace of three to five amperes per square foot. A few years ago "rapid nickel salts," claimed to permit of nickeling at two to three times the usual rate, were imported from Europe. These proved to be only mixtures capable of yielding more concentrated solutions than that enemy of progress, the "double sulphate," which for so long has masqueraded as the plater's friend. The American plater soon learned how to make up his own rapid solution, and as a result nickeling at ten to twenty amperes per square foot is very common today.

The most recent step in rapid nickeling, if nickel's twin-brother and rival, cobalt, may be included in this category, is the remarkable work of Kalmus and Barrows[1] in plating with cobalt at 150 amperes per square foot, turning out commercial plating of high grade in three minutes.

These achievements with cobalt suggested the desirability of obtaining similar effects with the cheaper nickel solution. In so far as the wonderful results of cobalt solution XIIIB depend upon its extreme concentration (312 grams of anhydrous cobalt sulphate, equivalent to 585 grams of the crystallized salt, per liter, or 7½ pounds per gallon) it should be possible to duplicate them with nickel, since its salts are equally soluble. It is in the matter of anode corrosion and in its absorption of hydrogen[2] that nickel is inferior to cobalt as a metal for electro-plating.

The nickel anode becomes "passive" on the slightest provocation, and instead of all of the current dissolving nickel as is desired,

[1] Trans. Am. Electrochemical Society (1915) 27, 75.
[2] *Idem.* (1915) 27, 121.

a portion of it is spent in producing acid at the anode. Besides cutting down the efficiency of deposition, this acid causes hydrogen to be evolved in considerable quantity on the cathode, where some of it is absorbed by the deposit. Absorption of hydrogen by nickel renders it hard and brittle, and is likely to cause it to curl away from the metal on which it is deposited. The addition of a small amount of some chloride to the sulphate solution usually used for nickel plating is a well-known remedy for this passivity of the anode.

Previous experience with hot nickel solutions indicated their use for overcoming the difficulties just mentioned, since in a hot solution anode corrosion is greatly improved and absorption of hydrogen is lessened.

A 25-gallon (95 liter) hot nickel bath was used at 125 to 150 amperes per square foot (14 to 16 per sq. dm.), with great satisfaction, producing in five minutes a heavier deposit than is obtained in an hour from the usual "rapid" bath at ten amperes per square foot. In spite of the extreme current density the deposits were superior in quality and adherence to ordinary nickel plate. Since the electrical instruments and current supply were inadequate for working this bath to its full capacity, a portion was removed to an enameled pail where it could be tested on small cathodes.

This solution contains nickel sulphate (single salt), nickel chloride, and boric acid in the following proportions:

	Grams / Liter	Oz. / Gallon
$NiSO_4.7H_2O$	240	32
$NiCl_2.6H_2O$	20	3
H_3BO_3	20	3

At the outset the anodes were the same that have been used in the plating laboratory for a number of years, *viz.*, strips of electrolytic nickel. Later cast anodes of the same material were employed. Results of some of these tests are presented in tabular form.

Exp.	Temperature C°	Temperature F°	Time Min.	Amperes per Sq. Dm.	Amperes per Sq. Ft.	Ampere-Hours per Sq. Ft.	Deposit
No. 10	67	153	5	31.7	295	24.5	Fine.
No. 48	71	160	5	47.6	422	28	Good.
No. 54	92	198	1	95.3	890	14.8	Fine.
No. 4	25	77	3	5.3	49	3	Fine.
No. 5	25	77	6	14	130	6.5	Mat, polishes well.

In no case was the deposit "burned." In No. 5 there was a vigorous evolution of gas, indicating a low current efficiency of deposition. Deposits from the hot solution were mat, but polished easily.

It is a matter of general observation that electrolytic deposits become rougher with increasing thickness; when comparing different plating baths it is therefore desirable to know the thickness of the deposits as well as their physical qualities. For the same current efficiency, the thickness of nickel deposited will be proportional to the ampere-hours per unit of surface. By a comparison of the ampere-hours per square foot in the accompanying tables, the relative thickness of different deposits may be estimated. At 100 percent efficiency one ampere-hour per square decimeter deposits 0.0123 mm., and 10 ampere-hours per square foot deposits 0.00052 inches, or 0.001 inch in thickness requires 19.2 ampere-hours. One hour at ten amperes per square foot, or ten ampere-hours, is considered good nickeling, and a common cobalt deposit by Barrows was 150 amperes per square foot for three minutes, or 7.5 ampere-hours. Judged by these standards the results shown in the tables are heavy deposits.

In order to secure samples from hot and cold solutions for direct comparison polished aluminum cathodes were used, from which the nickel was easily stripped.

DEPOSITS ON ALUMINUM.

Exp.	Temperature C°	Temperature F°	Time Min.	Amperes per Sq. Dm.	Amperes per Sq. Ft.	Ampere-Hours per Sq. Ft.	Deposit
No. 12	74	165	20	18.9	176	60.3	Fine, mat.
No. 14	35	95	12	11.7	109	22.6	Rolled up, brittle.
No. 15	38	100	22	8.2	76	27.9	Mat, tore in buffing.
No. 49	71	160	5	24.2	225	18.7	Fine.
No. 50	78	172	10	30.7	285	47.6	Fine. 0.002 inch (0.05 mm.) thick.
No. 53	98	208	25	15.2	141	60	Five successive deposits.

Plating on aluminum brought out the difference between deposits from cold and from hot solutions. An excellent deposit was obtained from the hot solution in every case, which bore polishing without peeling from the aluminum, and when stripped from the latter proved of excellent physical quality. Most of the deposits from the cold solution rolled up and partly separated from the cathode while in the plating bath, and in the few cases where this

did not happen the deposit was torn during polishing. No. 53 consisted of five successive deposits for five minutes, each coating being polished and immersed in the electric cleaner for ten seconds before re-plating. It is 0.0025 inch (0.06 mm.) thick, and is harder than the usual deposit from a hot solution.

Current efficiency tests were made by reading the current on a Weston model No. 280 ammeter, and determining the weight of metal deposited in five or six minutes. Since a difference of three seconds changes the weight of a five minute deposit by one percent, the results are subject to an error of at least this magnitude. Current efficiencies above 90 percent are obtained in the hot solution at 20 amperes per square decimeter (190 amp. sq. ft.). It is evident from the tests that heating the solution and lowering the current density raises the current efficiency.

CURRENT EFFICIENCY TESTS.

Exp.	Temperature C°	Temperature F°	Time Min.	Amperes per Sq. Dm.	Amperes per Sq. Ft.	Ampere-Hours per Sq. Ft.	Cathode Eff. Percent
No. 11	45	113	6	31.1	289	28.9	89.6
No. 13	29–40	84–104	6	31.1	289	28.9	19.4
No. 16	60–70	140–158	13	8.6	80	17.3	100.9
No. 46	25–28	77–82	5	19.4	180	15	31.7
No. 48	91–84	196–183	5	9.5	88	7.4	98
No. 51	77–73	171–163	6	26.4	245	24.5	100.5
No. 52	76–84	167–183	6	51.3	477	47.7	99.2

Polarization at the end of No. 52 was only 0.16 volt. Measurements of polarization at 70°C. (158°F.) gave 0.15 volt at current densities varying between 13 and 26 amperes per square decimeter (121-242 amp. sq. ft.). It is therefore probable that hot nickel solutions can be operated at high current densities with less anode surface than is at present used for current densities of 10 amperes per square foot.

In experiments with a solution containing 75 grams per liter (10 oz. per gallon) of the "double sulphate" two and a half times the current was required to cause burning at 70°C. (158°F.) that produced this effect in a cold solution, the weight of metal deposited being the same in the two cases. This indicates that concentration of metal is a greater factor in permitting the extremely high current densities used in these hot solutions than is the temperature. The beneficial effect of heating a nickel solution

consists in the improved quality of the deposit, and in better anode corrosion. To avoid convection currents the flame by which the solution was heated was removed at the beginning of each test. At the higher current densities there is noticeable heating of the solution by the current.

A nickel solution that is extensively used consists of the single sulphate, boric acid, and common salt. In order to learn if the substitution of common salt for the nickel chloride of the laboratory plating bath would cause any marked difference in its operation the following solution was tested:

	Grams / Liter	Oz. / Gallon
Single sulphate	240	32
Sodium chloride	30	4
Boric acid	22	3

TESTS OF BATH WITH SODIUM CHLORIDE.

Exp.	Temperature C°	Temperature F°	Time Min.	Amperes per Sq. Dm.	Amperes per Sq. Ft.	Ampere-Hours per Sq. Ft.	Cathode Eff. Percent	Deposit
No. 42	32	90	5	19	177	14.7	25.6	Good.
No. 43	71	160	5	19.6	184	15.3	82.3	Burned one edge.
No. 44	76	169	5	20.8	193	16.1	82.8	Burned one edge.
No. 86c	84	183	3	20.2	187	9.3	...	Fine.
No. 68d	78	172	4	25.3	234	15.6	...	Burned.

Although this solution gave fine results, it is inferior to the bath containing nickel chloride, in not permitting the use of so high a current density.

To make up the bath with nickel chloride proceed as follows: Dissolve the nickel salts in the proper amount of hot water, add nickel carbonate in small amounts at a time and heat until all acid is neutralized; either filter or allow to settle and decant the clear solution, and finally add the boric acid.

In so far as anode corrosion is concerned, any soluble chloride might be substituted for the nickel chloride, but not without some effect on the character of the deposit. Magnesium chloride or sodium chloride seems to be preferred for this purpose. In case either of these is used, neutralizing might well be done by the carbonate of the same metal. Ammonium salts and the "double sulphate" of nickel are to be avoided, since they are likely to cause crystallization from the solution when cold.

To obtain the best results from a hot solution the current density must be high; cables and tank rods must therefore be of ample capacity. Control of a hot solution by regulation of the amount of anode surface will probably be easier than in a cold bath. The heating coil should be of heavy lead (or hard lead) pipe, with a settling space of five or six inches below the lowest coil; lead will also serve as a lining for the tank. If an electric cleaner is operated from the plating dynamo, either the heating coil should be electrically insulated, or all rheostats should be connected on the cathode side of the line. Should gas pitting occur on first using the solution in the morning, it may be avoided by heating the bath to boiling for a few minutes before beginning plating. Seventy degrees centigrade (158°F.) is a good temperature at which to operate a hot nickel bath.

Owing to the peculiar properties of electrolytic nickel, the advantages of a hot over a cold solution are greater in nickel plating than in the deposition of any other metal.

ADVANTAGES OF A HOT OVER A COLD NICKEL SOLUTION.

1. Heating from 25° to 70° C. (79° to 158° F.) lessens the resistance of the solution one-half.

2. The current density may be increased two and a half to three fold.

3. The current efficiency, if less than 100 percent in the cold solution, is raised.

4. Anode corrosion is greatly improved, and higher current densities may be used at the anode as well as at the cathode.

5. The deposit is superior to ordinary nickel plate in toughness and freedom from peeling.

6. In the solution tested, plating may be done at 200 to 300 amperes per square foot (22 to 33 per sq. dm.), at which rate the same amount of metal is deposited in five minutes as requires one and a half hours in the "rapid solutions" now in use at ten amperes per square foot.

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DISCUSSION.

C. G. FINK: A year ago, at Atlantic City, Dr. Kalmus presented a paper on cobalt plating and the results he obtained, in particular with solution No. 13-B, were so remarkable, and the tests of the plating were so good, that many concerns have adopted cobalt in preference to nickel. Now Dr. Watts comes forward and saves the day for nickel.

PRESIDENT ADDICKS: I might repeat the remarks I made a few minutes ago on the other paper. It seems to me impossible to use in practice the rates of deposition recommended in the paper, and I would not think they would be commercial unless the power is almost an insignificant item. I suppose the plating plants have industrial power costing several cents a kilowatt-hour.

G. B. HOGABOOM: They are using this solution in a large plant in Wichita, Kansas, doing some work on lamp bodies, which are rotated very fast, about 1,000 r. p. m., and the deposit is very good. The cost is small considering the amount of work that can be turned out, but the disadvantage is that what is known as white nickel deposit, such as you see on stoves, cannot be obtained in hot solutions, the white in the deep parts has a tendency to turn yellow, which counts against it for such work.

J. C. WOODRUFF: The cost of current is small in the cost of plating. The baths are large, the amount of metal tied up in the anodes is considerable, and the cost of preparation of the surface and handling of the parts makes up a great deal of the total cost of the finished article.

G. A. ROUSH: The saving of time in turning articles out in a few minutes instead of an hour or an hour and a half, largely counterbalances the extra cost of power.

After the Atlantic City meeting last year, manufacturers in our neighborhood who do nickel plating asked me what I could tell them about the Kalmus proposition of cobalt plating, what I thought of its permanence, and the possibilities of its replacing nickel. I told them that I did not think it would replace nickel to any great extent, but that I thought the greatest factor would be the search for methods which would speed up the nickel plating

and make the nickel bath do the work they had expected cobalt to do.

J. W. RICHARDS: Your remark, Mr. Chairman, about the impossibility of such high current densities in practice does not apply to the ordinary plating bath, because it is a large bath with a comparatively small number of amperes going through it, as compared with a metal refining bath, which is absolutely full of anodes and cathodes. Furthermore, if it is desired to work at a temperature, of, say, 70° F. (21° C.), the current is useful in keeping the bath at that temperature, and if the bath became overheated a simple device could be used for reducing its temperature, as by circulating the solution outside and thus cooling the bath if it had a tendency to get too hot.

It is my impression that since the appearance of Dr. Kalmus's paper in our Transactions last year it has had a most important effect on the nickel plating industry, in speeding up the work. Mr. Hogaboom knows about that so much better than I do, that I would like to ask him if there has not been more or less of a revolution in the nickel-plating industry in the last year in that respect?

G. B. HOGABOOM: It is as Dr. Richards states; nickel plating is being speeded up, and is probably due directly to the deposits which can be obtained from the cobalt solution. However, cobalt solutions are not giving the satisfaction, generally, that is imagined; there are some drawbacks to it. You cannot get the white deposit. The deposit stains very rapidly, and does not have that pure whiteness that nickel has. If it is used on work that is to be heated like electric flat-irons it tarnishes very rapidly, and you cannot remove the tarnish. That works against it, and the price of cobalt is pretty high just now, $1.50 per pound.

JOSEPH W. RICHARDS: Has the fast nickel plating been satisfactory?

G. B. HOGABOOM: It has not been entirely satisfactory, because the solution becomes alkaline so rapidly that it gives the dull deposit. That is the disadvantage of hot nickel solutions. Just as soon as you get a solution alkaline, the deposit becomes dull; and if you keep it on the acid side, then the deposit is usually brittle, and will not adhere.

A. G. GIBBS: If there is any great gain in fast nickel plating the alkali could be removed as formed, by a little diaphragm cell placed in the circulating system. This operates commercially in another process.

O. P. WATTS (*Communicated*): In discussing the cost of power for rapid plating one important point appears to have been overlooked. Six volts is the standard pressure for plating dynamos, and in cold nickel solutions as now operated at 2 to 3.5 volts, 67 to 41 percent of the energy is wasted in the rheostat. So long as the plater gains the extra voltage needed for rapid plating by diminishing the resistance of the rheostat or entirely short-circuiting it, the additional power consumed in his plating tank is not costing him a cent; he is only utilizing energy which was formerly wasted. In most cases it will probably not be desirable to plate more rapidly than 70 to 100 amperes per square foot, for which 5½ to 6 volts should suffice. It was the purpose of this paper to acquaint platers with the possibilities of a hot, strong nickel solution for rapid plating; the particular temperature, concentration of solution and current density for the best results in practical plating can only be determined by experience.

It should be possible to maintain the necessary slight acidity by regulation of the anode surface, and of the amount of chloride in the solution. So far, with electrolytic anodes, my difficulty has been to prevent the bath from becoming too acid. This was overcome by putting in more anodes and by increasing the amount of nickel chloride.

When using a solution so acid that no nickel could be obtained from it at 20° C., heating to 70° C. caused a good deposit. The rise in temperature might be expected to cause an increase in the rate of corrosion of the deposited nickel, due to greater activity of the acid. Will some one explain the anomaly?

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, held in Washington, D. C., April 27-29, 1916.

TESTS OF TIN PLATING BATHS.

By Frank C. Mathers and Barrett W. Cockrum.

This work was undertaken at the suggestion of Dr. W. D. Bancroft, of Cornell University, who is chairman of a committee appointed by the American Electrochemical Society, in April, 1913, to investigate the problems of electroplating. Attention was directed towards tin on account of the great number of different baths for tin plating and the absence of any bath which is widely accepted by platers as satisfactory. This indicates that the baths, as described, do not produce satisfactory deposits.

The demand for the electro-deposition of tin is very small on account of the easily executed process of tin-coating metals by dipping in molten tin. However, the lack of a really satisfactory plating bath makes the amount of electro-deposition of tin still smaller.

Manipulation.

Each of the various tin baths described by Kern[1] in his review upon tin plating was prepared and electrolyzed at 0.4 amp. per sq. dec. (3.6 amp. per sq. ft.) under the prescribed conditions of temperature, acidity, stirring, etc. Two anodes of commercial tin, one on each side of the beaker, were suspended by iron wires in alkaline baths, by lead wires in complex baths where anode corrosion was good, and by platinum wires in the others. The baths were stirred occasionally with glass rods during the course of the electrolysis. The cathodes were of iron or thinly rolled pure tin. In each case electrolysis was continued constantly for two weeks, the cathodes being replaced by new ones whenever crystalline or spongy growths seemed to produce short-circuits.

[1] Trans. Am. Electrochem. Soc., 23, 199 (1913).

Classification of Tin Baths.

The baths for tin plating seem to fall into three principal classes, as follows:

1. Tin salts of mineral acids, with or without other inorganic salts or organic addition agents.
2. Alkaline baths, as sodium stannite, with or without other salts.
3. Complex or double salts.
4. Alkaline sulphides.

These latter were not tried in this work.

1. Tin Salts of Mineral Acids.

Many of the difficulties in tin plating are unavoidable because they lie in the specific inherent properties of tin salts and in the pronounced tendency of metallic tin to be electro-deposited in a loosely crystalline or a spongy condition. Stannous salts easily oxidize in the air with the formation of basic insoluble compounds, unless an excess of strong acid is present. The sulphate, being almost insoluble, and the nitrate, being unstable, cannot be used. This leaves, among the cheaper salts, only the chloride or the fluoride and no advantage seems to lie in the use of the more troublesome fluoride. A bath of stannic salts is reduced at the cathode by the current and a constant deposition of tin is not attained until a certain ratio of stannous to stannic salt is present, which ratio is theoretically the same as the ultimate composition of a bath made from stannous salts. Hence a solution of stannous chloride containing hydrochloric acid and perhaps such other salts as sodium chloride, ammonium chloride, etc., is the simplest and cheapest bath. Hydrofluoric, perchloric, fluoboric, and fluosilicic acids give soluble stannous salts, and they could be used for plating if they gave satisfactory deposits, although they are more expensive. An extensive study[2] has already been made in this laboratory of baths containing many combinations of tin salts of the mineral acids, both with and without organic addition agents, but in no case was it found possible to obtain a solid, firm deposit that was free from coarse or rough crystals. The deposits were masses of bright glistening crystals which adhered fairly

[2] Mathers and Cockrum: Trans. Am. Electrochem. Soc., 26, 133 (1914).

well in some cases. This class of baths is of no value where a solid, uniform deposit is desired, a fact that seems generally recognized, as is shown by the absence of baths of this kind among those recommended for plating purposes.

2. *Alkaline Baths.*

Tin salts readily dissolve in an excess of sodium hydroxide, forming a clear solution which remains free from precipitate and which would be satisfactory as the basis of a plating solution if such baths yielded firm, solid deposits. The voltage required by these baths is high, and the anode corrosion is low in many of them. A very large proportion of the tin baths which have been recommended for plating belong to this class, which may be further divided as follows:

(*a*) *Sodium stannite or potassium stannite, without the addition of other salts.* The baths[3] which were tried contained from 1.2 to 1.4 percent of tin as stannous chloride and from "sufficient alkali for a clear solution" up to 6 percent of potassium or sodium hydroxide. In all cases the deposits were masses of small, bright crystals which were worthless as a protective coating.

(*b*) *Sodium or potassium stannite and tartrates.* The addition of tartrates[4] to the alkali stannite baths did not improve the character of the deposit, which was spongy from the bath containing only 1.3 grams of fused stannous chloride per liter but crystalline from the bath containing 3 grams of the same salt per liter.

(*c*) *Sodium or potassium stannite and potassium cyanide, with or without other salts.* The various baths[5] are as follows:

KCN	K_2CO_3 or Na_2CO_3	$SnCl_2$ (cryst)	KOH or NaOH	SnO_2	$Na_2P_4O_7$ (cryst)	$Zn(C_2H_3O_2)_2$
1	82.5	...	5.5	17.5	...	1
10	...	11	to	...	...	...
1	80	1.5	dissolve	...	...	...
10	110	2.5	...	...	...	...
111	...	1.2	7.5	...	111	...
35	...	7.5	111	...	...	...

None of these gave good deposits of any considerable thickness. The following general observations were made:

[3] Baths Nos. 6, 7 and 8 in Kern's Report. *Loc. cit.*
[4] Baths 9 and 10 in Kern's Report. *Loc. cit.*
[5] Baths 11, 12, 13, 14, 15 and 16 in Kern's Report. *Loc. cit.*

(*1*) With large amounts of carbonate and little or no sodium hydroxide, the anodes dissolved so poorly that the tin in the bath was soon exhausted, after which both electrodes gassed vigorously. These baths gave good looking, bright deposits which were very thin however. The current yields were very low, as was indicated by the quantity of gas evolved at the electrodes. It would require an extremely long time to obtain a deposit of any reasonable thickness from such a bath.

(*2*) Potassium cyanide seemed to be without much influence upon the crystalline structure of the cathode.

(*3*) Very large amounts of the potassium cyanide must be accompanied by correspondingly large amounts of sodium hydroxide, otherwise the tin is precipitated as a sludge in the bath and, upon electrolysis, little tin is deposited upon the cathode.

A bath containing 9 percent potassium hydroxide, 0.35 percent potassium cyanide, 0.75 percent potassium bitartrate, and 0.75 stannous chloride is used commercially[6] in barrel plating. The bath is run hot (70°C.) and a thin deposit is obtained. At intervals more of the potassium cyanide must be added. Experiments with this bath in a still solution indicated that thick deposits could not be obtained because of the formation of projecting crystals. However, very thin deposits appeared to be good, because the crystals were too small to be readily seen. The tumbling in the barrel would compact the deposit into a more firm and solid coating.

(*d*) *Sodium stannite and sodium thiosulphate.* The baths[7] contained, in percent, as follows:

$Na_2S_2O_3$	NaOH	$SnCl_2$	NaCl
7.5	12.5	5	...
6	12.	3	...
1.5	9	3	1.5

The baths with 6 percent or more of the sodium thiosulphate gave firm, finely-crystalline deposits, which became rough on continued electrolysis. A fine black precipitate was formed in the bath when the sodium thiosulphate was added. The deposits from these baths were the best obtained from any bath described by Kern. The deposits were dark but became bright and metallic after buffing. On continued electrolysis the deposits became rough

[6] Private communication.
[7] Baths 17, 18 and 19 in Kern's Report. *Loc. cit.*

and nodular, but projecting roughly adhering crystals were absent. Solutions at room temperature worked better than at 60°C. (140° F.). The voltage was 1.2.

3. Complex or Double Salts.

(*a*) *Pyrophosphates.* The Roessler bath,[8] or modifications of it containing 1 to 3.7 percent of sodium pyrophosphate and 0.1 to 2 percent of fused stannous chloride, is highly recommended by various writers. The deposit from a hot solution is said to resemble silver. We are aware that this bath is used commercially, but nevertheless the deposits in our experiments were spongy and non-adherent. It seems that only thin deposits are produced, and that tumbling or scratch-brushing must be resorted to in order to give the deposits a bright, metallic appearance. Two of these baths, which are used commercially,[6] are:

(*1*) Six parts of sodium pyrophosphate to 1 part of fused stannous chloride. It is said that the concentration can vary within rather wide limits without affecting the deposit very much.

(*2*) Three percent sodium pyrophosphate, 0.75 percent fused stannous chloride and 0.2 percent alum.

It is claimed that these baths may be run either hot or cold, but that only a low current must be used. It is recommended that a saturated solution of fused stannous chloride in sodium pyrophosphate be added at intervals to compensate for poor anode corrosion.

(*b*) *Stannous Ammonium Oxalate.* A deposit consisting of long, needle-like crystals was obtained from a bath[9] containing 2 to 3 percent stannous chloride, 5.5 to 6.5 percent ammonium oxalate and 0.3 to 0.4 percent oxalic acid. The completed bath was heated to boiling before using. The addition of peptone[10] to a modification of this bath containing more tin, prevented the formation of loose crystals and produced by far the smoothest, firmest and thickest deposit of tin which was obtained from any tin bath.

(*c*) *Acid Tartrate.* A bath[11] containing 6 percent potassium hydrogen tartrate and 1.5 percent stannous chloride gave a mass of small, loosely adherent crystals. After two weeks of continuous

[8] Bath 2 in Kern's Report. *Loc. cit.*
[9] Bath 1 in Kern's Report. *Loc. cit.*
[10] See Mathers and Cockrum: Trans. Am. Electrochem. Soc., **29**, 411 (1916).
[11] Bath 5 in Kern's Report. *Loc. cit.*

electrolysis, the crystals became much smaller and showed a tendency towards sponginess. The anodes dissolved unevenly.

Tinning by Contact.

The various dip or immersion solutions for tinning by contact without the use of outside current gave bright deposits of tin, thereby confirming all that is said of them in the literature and in the books upon plating.

SUMMARY.

The various baths for tin plating, which were described by Kern,[1] were prepared and electrolyzed for two weeks with a current density of 0.4 amp. per sq. dec. (3.6 per sq. ft.) under the conditions recommended.

In no case was a satisfactory deposit obtained, although the sponsors for the various formulas have made roseate claims for them. In most cases the deposits were masses of more or less adherent crystals, although in some cases they were spongy.

Among the baths described by Kern, the Beneker bath[12] containing 25 gms. of sodium hydroxide, 10 gms. stannous chloride and 15 gms. of sodium thiosulphate in 200 cc. of water, gave the smoothest, firmest deposits of good thickness. The deposits were dark in color but could be scratch-brushed to a bright, metallic appearance. The bath seemed to gradually deteriorate, the deposit becoming black and at last non-adherent. This bath is considered to be far below the quality desired for electroplating.

Some of the baths containing combinations of potassium cyanide and alkali carbonates or hydroxides with a little stannous chloride gave bright deposits, but there was a simultaneous liberation of hydrogen, and anode corrosion was poor. Such thin flashings hardly deserve the name of tin plates.

The stannous ammonium oxalate bath containing peptone as an addition agent[10] gave a smooth, firm, finely-crystalline deposit, the best obtained from any bath.

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[12] U. S. P. 921,943; Met. Chem. Eng., 7, 285 (1909).

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PEPTONE AS AN ADDITION AGENT IN STANNOUS AMMONIUM OXALATE BATHS.

By Frank C. Mathers and Barrett W. Cockrum.

The statement was made in the previous paper[1] that the best tin deposit was obtained from a stannous ammonium oxalate bath containing peptone as an addition agent, the use of which was discovered in this laboratory. Without the peptone the deposit is of no value as a protecting coat, because it consists of projecting needle-like crystals.

The effect of the peptone (Witte's) was remarkable. As soon as it was added, the tendency to form the projecting, loosely adhering crystals ceased and the deposit became so smooth and finely crystalline that thick cathodes (0.5 to 1 cm. thick) could be prepared, and so firm and coherent that shavings of tin could be cut from the deposit with a knife.

Clove oil, glue, gelatine and formin, agents which have been found effective with other metals, were practically without any beneficial influence in preventing the formation of the crystals. Licorice extract and aloes residue[2] prevented the formation of loose crystals but peculiar club-like projections formed on the cathodes.

Carbon disulphide, even in small amounts, made the deposit spongy and non-adherent, a condition which persisted until the carbon disulphide was exhausted, when the deposit again became crystalline. There was no intermediate time when a non-crystalline, solid deposit was obtained. The carbon disulphide was different from the other addition agents, none of which produced a spongy deposit.

[1] Mathers and Cockrum: Trans. Am. Electrochemical Soc., **29**, 405 (1916).
[2] Trans. Am. Electrochem. Soc., **27**, 131 (1915).

Manipulation.

The experiments were conducted as described in the previous paper.[1] The active area of the anodes was 32 sq. cm. and of the cathode 50 sq. cm. The volume of the bath was 300 cc. A current density of 0.4 amp. per sq. dec. (3.6 amp. per sq. ft.) was used. The anodes were amalgamated, to keep the anode slime out of the bath. The baths were stirred occasionally. Impurities in the anodes sometimes caused the formation of an insoluble coating which had to be removed mechanically.

Concentration of the Baths.

The addition of 0.1 to 0.5 percent peptone to the bath containing 2.5 percent stannous chloride, 5.5 percent ammonium oxalate and 0.3 percent oxalic acid (the composition generally recommended) gave a smooth, firm deposit on the bottom of the cathode but the top part was dark, clearly showing that the bath did not contain enough tin. Solutions materially more concentrated than the above formed crystals of a salt in the bath, a trouble which was greatly lessened by starting with stannous oxalate in place of the stannous chloride, whereby the ammonium chloride was eliminated.

The result of numerous experiments showed that a very satisfactory concentration and composition was 5 percent stannous oxalate, 6 percent ammonium oxalate, 1.5 percent oxalic acid and 0.25 percent peptone, as compared with 2.28 percent stannous oxalate, 4.14 percent ammonium oxalate and 0.3 percent oxalic acid for the original bath.[3] The principal advantage in using the increased amount of oxalic acid is that it prevents the "crawling" of the solution up the sides of the beaker, owing to the capillary action of porous crystalline salts. Larger amounts of oxalic acid, 7 to 10 percent, caused the formation of hard crystals of a stannous salt upon the electrodes. Acetic acid may be used in place of the oxalic, but it showed no advantage. A higher concentration, 7.5 percent stannous oxalate and 9 percent ammonium oxalate, caused more trouble from "crawling" and from the formation of crystals of salt. More ammonium oxalate than is required to dissolve the stannous oxalate and to keep the anodes

[3] Bath 1 of Kern's Report. Trans. Am. Electrochemical Soc., 23, 199 (1913).

clean is not desirable, because it greatly promotes the formation of salt crystals in the bath. Variation in the quantity of peptone was without much effect, but 0.1 percent gave a rougher deposit than 0.25 percent, the quantity which is recommended.

Maintenance of the Bath.

Continuous electrolysis of the bath produces a decrease in the concentration of tin, free oxalic acid and peptone. This decrease in the concentration of tin shows itself after a time by the darkening of the deposit, which finally becomes black and non-adherent and, at last, gas is evolved from the cathode. The addition of stannous oxalate immediately causes the deposit to become bright and coherent again, thus clearly showing that the trouble was caused by lack of tin.

The anodes, if they have become covered with a coating of insoluble material, must be washed with a brush until the pure tin is again exposed, and more ammonium oxalate should be added to the bath.

During electrolysis, a fine yellow precipitate forms in the bath and settles to the bottom as long as sufficient oxalic acid is present, but if the bath needs more oxalic acid, porous crystalline salts form on the sides of the beaker and on the electrode connections at the surface of the liquid, and gradually climb upward. The addition of more oxalic acid stops this.

More peptone must be added whenever the deposit shows projecting crystals.

Baths run at 50° C. (122° F.) required more doctoring than those at room temperature and the crystalline structure of the deposits was more pronounced.

In spite of these additions to the baths, they finally became so deteriorated that bright solid deposits could no longer be obtained.

Current Density.

A good deposit was obtained at 0.8 amp. per sq. dec. (7.4 amp. per sq. ft.). However, the experiments described in this paper were run at half that density. The voltage averaged about 0.5 with the cathode midway between the two anodes, which were 4 cm. apart.

Other Salts in the Baths.

Potassium stannous oxalate is less soluble than ammonium stannous oxalate, hence potassium oxalate cannot be used in place of the ammonium oxalate. Potassium and ammonium chlorides were not desirable additions, on account of their tendency to form crystalline salts.

Character of the Deposits.

Some of the cathodes, when heated just a little above the melting point of tin, swelled and foamed, and the vapor which was given off burned, thus showing the occlusion of considerable amounts of organic material. A porous, foam-like mass of metal remained if the heating was discontinued at the proper time.

CONCLUSIONS.

The addition of peptone to the stannous ammonium oxalate bath is essential for the production of a thick, smooth, finely crystalline deposit of tin. No other tin bath (except possibly the sulphide, which was not tried) is known from which such a thick, smooth deposit can be obtained.

A good composition of bath is: 5 percent stannous oxalate, 6 percent ammonium oxalate, 1.5 percent oxalic acid and 0.25 percent peptone. The stannous oxalate may be easily made by precipitating a solution of stannous chloride with oxalic acid.

The bath was run at room temperature at 0.4 amp. per sq. dec. (3.6 per sq. ft.). The solution must be stirred at intervals.

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DISCUSSION.

PRESIDENT ADDICKS: I do not know anything about tin plating, but wish to say something about the refining of tin. The field of tin plating seems quite narrow, as stated in the paper, and it is really more of academic interest than anything else, but the refining of tin is a different matter. This country for years has been a large user but a non-producer of tin; all the large supplies of tin from South America have been sent to England or Germany for refining, and then back here. I had some experience on a committee trying to draw up specifications for tin. It is sold almost entirely on reputation, and practically without relation to its purity. Just at the present time American engineers are going into the field, shipping tin concentrates here, smelting them, and electrolytically refining the tin; the first electrolytic tin is just appearing on the market.

WILLIAM BLUM: Not in special reference to this paper, but on the general subject of the solutions for electroplating, I would like to urge that concentrations be expressed, not in percent but in grams per liter, since they are always so determined in analysis, and as a rule the solutions are prepared in that way. If you do not know the density of the solution, you cannot conveniently make up the solution on a percentage basis. As a matter of fact when an author says "10 percent," he usually means 100 grams per liter, and not 10 percent by weight.

G. A. ROUSH: As I understand Dr. Mathers' work his idea is to work up a solution from which we can get heavy coatings of metal, such as would be desired in refining baths, and not use them in commercial plating, as commercial plating with tin is, so far, a small matter.

I made up some of these baths of the composition recommended, with the addition of peptone, and tried them out in the same way they would be used for commercial plating purposes, to make a thin deposit. I found that they worked satisfactorily and that we could use current densities several times those stated in the paper,

in fact, up to four or five times that amount, and still get perfectly satisfactory results for plating of ordinary commercial thickness.

J. W. RICHARDS: I would call attention to one of Dr. Mathers' samples. It is a small piece of nickel anode which has been hung in the bath by a strip of lead. The anode is strongly corroded, but the lead strip is intact.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, held in Washington, D. C., April 27-29, 1916.

ADDITION AGENTS IN THE ELECTRO-DEPOSITION OF SILVER FROM SILVER NITRATE SOLUTIONS.

By Frank C. Mathers and John R. Kuebler.

AIM AND RESULT OF THIS INVESTIGATION.

The aim of this research was to study the action of addition agents in restraining the characteristic, loosely adherent, crystalline structure of silver electro-deposited from silver nitrate solutions and, if possible, to discover a method of depositing solid, smooth and adherent silver cathodes.

The ordinary addition agents such as glue, peptone, clove oil, aloin, etc., were found to be either without appreciable effect or to prevent only partially the formation of crystals and in no case was a thick, smooth deposit obtained.

Tartaric acid was far superior to anything else that was tested. A bath containing three percent each of silver as nitrate, nitric acid and tartaric acid gave a smooth, hard and entirely adherent silver cathode.

By the simultaneous addition of 0.01 percent of glue every twelve hours, the amount of tartaric acid could be reduced to about 0.4 percent.

MANIPULATION.

Small beakers containing 100 cc. of the electrolyte were used as electrolyzing vessels. The electrolyte contained 3 percent of silver as silver nitrate and 3 percent of free nitric acid. Square pieces of pure sheet silver about 0.2 mm. in thickness and having a total area of 25 sq. cm. were used as cathodes. Anodes, also of pure silver, were melted in cupels with a blast lamp and a hole was made in each one by a small piece of wood which was thrust through the center of the molten silver. Two anodes, suspended by platinum wires, were suspended in each beaker. A current density of 0.8 amp. per sq. dec. (7.4 amp. per sq. ft.) was used. Each bath was continuously but gently stirred by a slow current of air bubbles from a glass tube which was drawn to a capillary at the end in the bottom of the bath.

ADDITION AGENTS OF THE USUAL CLASS.

Some of the addition agents such as clove oil, peptone and pyrogallol are oxidized by the free nitric acid with the formation of colored solutions whereby the action of the material is probably changed.

Glue, 0.02 to 0.04 percent, greatly lessened the crystalline structure. The projecting crystals upon the edges and at irregular places on the faces were fairly adherent. With increasing quantities of glue, vertical striations formed and finally with 0.26 percent, a spongy deposit was produced.

Peptone (0.04 percent was best) gave a striated, finely crystalline deposit of a white color but with projecting, crystalline edges. The deposit was better than the one with glue. An excess of either glue or peptone made the deposits spongy.

Gum Arabic slightly lessened the tendency to form crystals, but aloin and clove oil seemed to be practically without effect.

Pyrogallol and tannin, 0.05 percent, each produced a fluffy, voluminous, tinsel-like deposit which was easily shaken from the starting sheet.

The almost total failure to obtain smooth deposits with the above addition agents which are so successful with other metals, indicated the importance of trying unusual classes of addition substances.

INORGANIC ADDITIONS TO THE BATHS.

Orthophosphoric acid, 1 to 10 percent in baths containing 1 to 3 percent nitric acid, did not materially reduce the tendency to form crystalline deposits but in some cases the deposits seemed more adherent. Without free nitric acid, spongy deposits were obtained with the higher concentrations of the orthophosphoric acid.

Metaphosphoric acid, 1 to 2 percent and no free nitric acid, gave hard, firm, apparently non-crystalline, vertically striated deposits of a brownish color. Addition of nitric acid made the deposits slightly crystalline in appearance and of a white color. One percent of metaphosphoric acid and 3 percent of nitric acid seemed best. These baths gradually deteriorated, the deposits becoming more loosely crystalline. Except for this difficulty, this type of bath might be made satisfactory. See Fig. 1, No. 1.

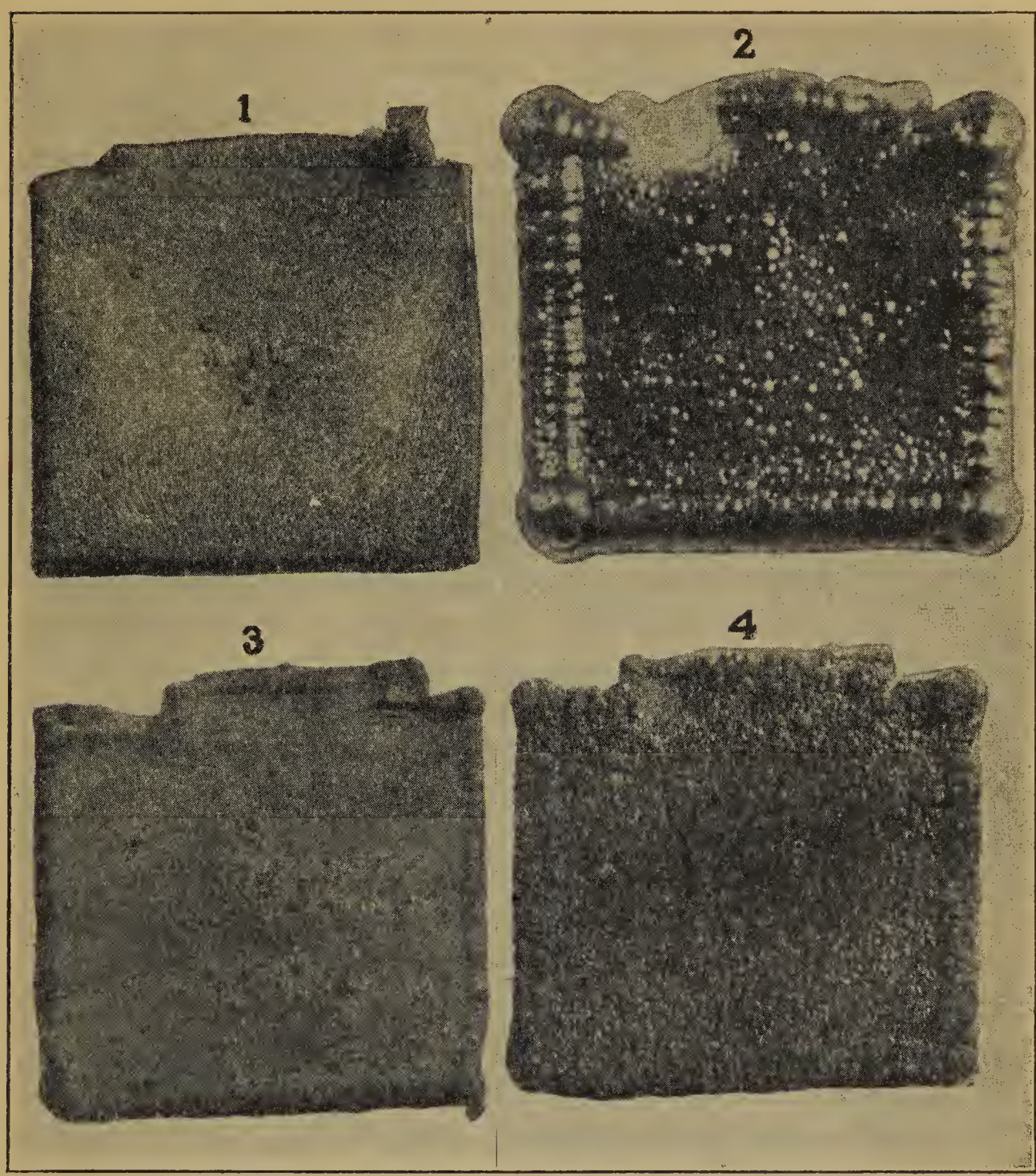


FIG. 1.

1. 4.8 percent silver nitrate, 3 percent nitric acid and 1 percent metaphosphoric acid.
2. 9.6 percent silver nitrate, 3 percent nitric acid, 3 percent tartaric acid and 2 percent ferric nitrate.
3. 4.8 percent silver nitrate, 0.7 percent nitric acid, 0.35 percent tartaric acid and 0.01 percent glue twice daily.
4. 4.8 percent silver nitrate, 3 percent nitric acid and 0.2 percent tartaric acid.

Boric acid produced no improvement.

The addition of 2 percent of the nitrates of ammonium, sodium, potassium, barium, strontium, calcium or magnesium, or 10 percent of the nitrates of sodium, calcium or strontium produced no beneficial results.

ORGANIC ACIDS IN THE BATHS.

One percent of oxalic acid and 3 to 10 percent of nitric acid (the increased nitric acid was to redissolve the precipitate of silver oxalate) gave a spongy deposit. With 0.006 percent of oxalic acid and 3 percent of nitric acid no precipitate was formed in the bath but the deposit, which was finely crystalline and smooth in the beginning, gradually formed crystalline projections.

Succinic acid gave about the same results as the oxalic.

Lactic acid, 1 to 5 percent, and nitric acid, 1 to 3 percent, gave crystalline deposits. The higher the percentage of lactic acid, the smoother were the deposits. These deposits seemed as rough and coherent as those with the glue alone.

Picric acid, 0.5 percent, gave spongy deposits.

Tannic acid in small quantities gave loose, tinsel-like crystals. Larger amounts of tannic acid (0.5 percent) with 1 percent of nitric acid gave spongy deposits.

Citric acid, 3 percent, gave firm, dark, lustrous deposits which were free from any indications of loose crystals. The effect was similar to that with tartaric acid except that the latter was more permanent and showed less tendency to make the deposits spongy.

Tartaric acid was the best addition agent found.

TARTARIC ACID AS AN ADDITION AGENT.

Concentration of the Baths. Three percent of silver as nitrate was chosen because the commercial refining baths have about this concentration. The increase in the concentration of the silver to 6 percent very much improved the deposits, which became smoother especially on the edges. Increased cost would be the only objection to this higher concentration of silver.

The higher the percent of nitric acid (0 to 1 percent), the more pronounced was the crystalline structure when low concentrations of tartaric acid (0.2 to 1 percent) were used. Continuous electrolysis of baths low in nitric acid (a few drops to 0.5 percent) finally produced poorly adhering deposits. This trouble could be avoided by adding more nitric acid at intervals. Three percent of nitric acid, the quantity used in most of these experiments, was chosen in order to avoid the necessity of making these repeated additions. If a lower concentration of nitric acid had been chosen and maintained, a lower percent of tartaric acid

would have given as good deposits as the higher percent which was used in these experiments.

Deposits from baths with the tartaric acid varying from 0.1 to 8 percent were at first equally good as regards smoothness and firmness. The color varied from a light grey to a dark grey as the quantity of tartaric acid was increased. As electrolysis progressed this color gradually faded, becoming pure white in those baths containing the smaller amounts of tartaric acid and lighter grey or even merely slightly purplish in spots in those baths having the larger quantities of tartaric acid. The length of time the cathodes remained smooth and free from rough crystalline projections was directly proportional to the quantity of tartaric acid present. See Fig. 1, No. 4. Three percent of tartaric acid was considered best; the greater smoothness produced by the larger quantities was not deemed sufficient to warrant the additional cost.

Use of crude cream of tartar. Crude argols cannot be added directly to the baths on account of the large quantity of insoluble matter and the aqueous extract cannot be used because it contains substances which produce sponginess. However, the crude potassium bitartrate, obtained by crystallization of the aqueous extract from argols, gave as good deposits as refined tartaric acid except that they were a little rougher.

Effect of temperature. Increase in temperature increased the formation of crystals. The deposit at 50° C. from a bath containing 3 percent tartaric acid, was as crystalline as the deposit from a bath with 0.5 percent tartaric acid at room temperature (23° C.). In the beginning a darker, smoother, more shining deposit was obtained at 13° C. than at room temperature, but the final cathode did not seem to be materially better.

Current density. An increase in current density to 1.6 amp. per sq. dec. (14.8 amp. per sq. ft.) caused the cathode to become much rougher, some of the projections being easily broken off.

Firm, comparatively smooth deposits were obtained with higher currents from vigorously stirred solutions or from baths containing a higher percent of silver.

Use of impure anodes. The use of anodes containing base metals, as lead, copper, zinc, etc., causes a decrease in the concen-

tration of silver in the bath because the amount of silver deposited upon the cathode is equivalent to the total quantity of metals dissolved from the anode of which only a portion is silver. With a 3 percent silver solution and 900 fine anodes, between 5 and 6 ampere hours per 100 cc. of solution practically exhausts the silver in the electrolyte providing none of the base metals are deposited. To avoid this difficulty, silver nitrate must be added at intervals in sufficient quantity to maintain the desired concentration. Observing this precaution with a bath containing 6 percent silver as nitrate, and 900 fine anodes, a cathode weighing 175 grams was deposited from a 100 cc. bath. The cathode was exceptionally smooth and was free from irregular projecting places on the edges. At the end of the electrolysis, the bath contained 16 percent of base metals as calculated from the weight of anodes dissolved. In commercial refining, baths are discarded or purified when the impurities reach 4 percent in some systems or 8 percent in others.

Effect of inorganic substances in baths containing tartaric acid. The deposits were made less firm and less solid by sodium or magnesium nitrate, more rough by copper nitrate, less rough by lead nitrate and were unchanged by zinc nitrate. These nitrates of the heavy metals showed such a small influence upon the deposits that other conditions might have been responsible for the small variations noted.

Ferric nitrate (2 percent) made the deposit very much smoother and darker in color. The smoothest cathode obtained in the work was from a bath containing 6 percent of silver, 3 percent of tartaric acid, 3 percent of nitric acid and 2 percent of ferric nitrate. The cathode looked and felt like a piece of polished, dark metal. Chromium and aluminum nitrates did not show this same action. See Fig. 1, No. 2.

Sulphuric acid (0.5 percent) seemed to partly neutralize the effect of the tartaric acid. The deposit was as crystalline as if a much smaller quantity of tartaric acid had been used.

Metaphosphoric acid did not improve the deposits but it had an action as shown by the striations.

Organic addition agents in the baths containing tartrates. Aloin and clove oil seemed without effect. B-naphthol made the deposit non-adherent.

Peptone (0.04 percent with 0.25 percent tartaric acid) gave a smooth, brownish colored, glistening deposit in the beginning, but the deposit gradually became less firm and finally became spongy.

The addition of 0.02 percent of glue twice daily caused the deposit to have a dark, shining, metallic appearance in the beginning but this metallic luster gradually changed to a mat surface. When 0.46 percent of glue had been added the deposit became partly spongy. This is the usual result when an excess of organic matter is present. The use of glue is recommended on account of the greater smoothness which it produces.

Good deposits were obtained by the addition of small amounts of glue to baths containing less than 3 percent of the tartaric acid. A firm but slightly rough deposit was obtained from a bath containing 0.25 percent of tartaric acid to which 0.01 percent of glue was added twice daily. After 56 grams of silver per 100 cc. of the bath had been deposited, some crystalline projections formed, an indication of the exhaustion of the tartaric acid. A firm, comparatively smooth deposit, weighing about 100 grams per 100 cc. of bath, was obtained from a bath containing 0.5 percent of tartaric acid to which 0.01 percent of glue was added twice daily. It was necessary to add more tartaric acid to this bath before another smooth deposit could be produced. The exhaustion of the tartaric acid was shown by the crystalline structure and the white color of the deposit which, however, was still tough and adherent.

A smoother deposit was obtained from the baths containing the glue and the smaller amounts of tartaric acid by using only 0.5 percent of nitric acid. More nitric acid should be added when the bath becomes dark colored. See Fig. 1, No. 3.

Cost of the addition agents. With tartaric acid at 30 cents per pound and glue at 20 cents per pound[1], the cost of these addition agents is 0.17 cent per pound (0.37 cent per kilo) of silver deposited. This assumes that 0.5 percent of tartaric acid and a total of 0.1 percent of glue are required and that only 100 gms. of silver are deposited from each 100 cc. of electrolyte. With 900 fine anodes, the bath would then contain over 8 percent base metal impurities and would have to be purified or discarded. The cost at present prices would be 0.23 cent per pound. These

[1] List prices before the war.

prices are for purified tartaric acid, whereas a crude cream of tartar gives satisfactory results.

Vigorous stirring of the baths. A current of 2.4 amp. per sq. dec. (22.2 amp. per sq. ft.) was used in baths which were vigorously stirred with rotating glass stirrers. The edges of the cathodes became thick and projected somewhat, but this was almost prevented by increasing the concentration of the silver to 6 percent. However, smoother, more shiny deposits were obtained by using 0.08 percent of glue (added in four portions) and 0.5 percent of tartaric acid. A somewhat smoother deposit was obtained by using greater quantities of tartaric acid.

Properties of the deposited silver. a. Color. The dark, shiny color which was always noted in the beginning of each electrolysis gradually changed to white, except in the presence of ferric nitrate or repeated additions of glue in which cases the dark color persisted to the end.

b. Smoothness. In all cases the deposits became less smooth as electrolysis progressed. Ferric nitrate aided materially in maintaining the initial smoothness.

c. Hardness and structure. The deposits were hard but brittle. Cathodes only 0.5 cm. thick could not be broken by the hands but cracked into many pieces when struck with a hammer. Pieces from some of the cathodes showed distinct strata.

d. Occluded material and specific gravity. When heated, the cathodes swelled, becoming a fourth larger in some cases, and the deposited silver crumbled from the starting sheet, giving a great number of small, loose pieces of silver, if the temperature was kept below the melting point of silver. An odor of burning tartaric acid could be detected in some cases and if the deposit was dark, grey or shiny, the coloration disappeared and the mass assumed a silver white color.

The darker, smoother and more shiny the cathodes, the greater was the quantity of occluded material. Some analytical results are as follows:

Description of cathode.	Percent loss on drying at 160° C.	Percent loss from 160° C. to ignition with a Meker burner.
White, slightly crystalline	0.13	0.77
White, smooth	0.28	0.99
White. No swelling when heated	0.15	0.23
Shiny and smooth	0.64	1.22
Shiny and smooth	...	1.16

The loss at 160°C. seemed to be influenced by the length of time the samples had been air dried. All of the above samples were from baths containing tartaric acid but no glue.

The density of the air dried samples which were mechanically removed from the starting sheets varied from 9.84 for dark shiny samples to 10.07 for crystalline ones. After ignition until the sample had expanded to maximum volume and the color had become silver white, the apparent specific gravity of a shiny sample was as low as 8.8. The specific gravity was raised to 9.37 by putting the pycnometer under reduced pressure which caused a vigorous evolution of bubbles from the pieces of silver. This shows that the escape of the occluded substances during the heating puffed the silver into minute gas chambers. The specific gravities of different cathodes did not agree, due to the influence of the conditions of electrolysis which affected the quantity of occluded material and also to the effect of the temperature and time of heating and the size of the pieces of silver.

Current efficiency at the cathode. A bath containing 3 percent of silver as nitrate, 3 percent of nitric acid and 3 percent of tartaric acid gave a cathode efficiency of 101.8 as compared with a silver nitrate coulometer and 101.82 as compared with a copper coulometer. This shows 1.78 percent of impurities in each 100 grams of deposited silver, a number approximately equal to the loss on ignition for shiny silver given above.

REVIEW AND DISCUSSION.

About 10 percent of the silver output is electrolytically refined in solutions of silver nitrate containing nitric acid. For the most part, the silver is deposited in the well-known crystalline, non-adherent condition. There are many advantages in the deposition of the silver in a solid coherent form[2]. Chemists at the United States Mint at Philadelphia devised the improvement of adding 0.008 to 0.01 percent of glue[3] to the baths each day, whereby the cathode deposits were less crystalline and were coherent enough that vertical cathodes could be used and handled in the way ordinarily followed in electrolytic metal refineries. A c. d. of 8 amp. per sq. ft. (0.9 per sq. dec.) was used. The

[2] Betts, Trans. Amer. Electrochem. Soc., 8, 121 (1905); Easterbrooks, *ibid.*, 132.
[3] Annual Rep. of Director of U. S. Mints, 1905; Met. Chem. Eng., 4, 307.

cathodes, as shown by a cut of a photograph[3], were rough and crystalline and in no way comparable in smoothness with the cathodes obtained in this research by the use of tartaric acid. The use of glue which was adopted by other of the United States Mints[4] has now been discontinued because it was of little value at the higher c. d. of 15 amp. per sq. ft. (1.6 amp. per sq. dec.), which was necessary for the sake of speed. It is said that the crystalline silver cathodes, without the use of any organic material, are coherent enough that they can be withdrawn from the baths if sufficient care is exercised.

This same action of glue in restraining the crystallization of the silver has been noted in silver nitrate solutions containing traces of nitric acid,[5] in pure silver nitrate solutions containing no free nitric acid or other impurities[6], and in these same solutions using rotating cathodes[7].

Tannin, pyrogallol and resorcinol are of no value and an excess makes the deposits non-adherent[5].

Organic impurities of many kinds in pure neutral silver nitrate solutions were found[6] to affect the character of the silver deposit which was "non-crystalline or imperfectly crystalline, depending upon the quantity of the impurity present." The things tried were: aqueous extract from various kinds of paper—filter, writing, blotting, rag and wood, pine wood shavings, silk, cotton and linen. The same effect was produced by glue, by Bredig's colloidal silver and by one percent additions of the following: hydrazine, hydroxlyamine, dextrose, invert sugar, formaldehyde, acetaldehyde, furfuraldehyde, benzaldehyde, phenol, resorcinol, hydroquinon, and phloroglucin. All of these substances which affect the silver deposit have the power of reducing solutions of silver nitrate to colloidal silver. Silver nitrite, silver hyponitrite, starch and cane sugar were without action on the silver deposit and they do not form any colloidal silver in the baths. The theory is advanced that the colloidal silver is the essential thing and that each particle of this colloidal silver which is deposited upon the cathode becomes a nucleus for a new silver crystal, hence the deposit becomes a mass of very small crystals rather than a much

[4] Eng. Min. Journ., **92**, 901.
[5] Jarvis and Kern, School Mines Quart., **30**, 100.
[6] Rosa, Vinel and McDaniel, Bull. Bur. Standards, **9**, 209.
[7] Snowden, Trans. Amer. Electrochem. Soc., **7**, 143.

smaller number of large ones. Moreover, all deposits, where the addition agent has shown an action, are heavier than required by Faraday's Law. A weakness in this theory is that it cannot apply to solutions containing free nitric acid which would prevent the reduction to colloidal silver but the presence of the nitric acid does not prevent the action of the glue and other substances in restraining the crystallization of the silver deposit.

In the separation of silver from antimony, the silver has been deposited from solutions containing silver nitrate, nitric acid and tartaric acid in a non-weighable form[8] and in a "faultlessly crystalline condition of silver luster."[9] The action of the tartaric acid in restraining the crystallization of the silver was apparently overlooked, probably because the experiments were run, for the most part, in warm solutions, a condition which partly prevents the action of the tartaric acid.

Nitric acid or calcium nitrate in pure silver nitrate solutions increased the number of crystals in the silver deposit. Silver acetate increased the number of crystals 100 times, the deposit being like a "surface of frozen snow."[6] Ammonium acetate was found to improve the deposits for quantitative work.[10] These results show that the acetate radicle is partly effective as an addition agent if we accept the idea that the function of an addition agent is to make the crystals very small and coherent but not so small nor so impure from absorbed addition agent that the deposit becomes spongy and non-adherent.

All of the organic acids tried in this work had an influence on the deposits which in most cases were made more finely crystalline and coherent. Only tartaric and citric acid gave smooth deposits showing little or no crystalline structure. These organic acids, tartaric, and to a lesser extent citric, acted very differently from the ordinary colloids. One important difference is the beneficial effect of large amounts of the tartaric acid while any excess of glue and other colloids or of some of the organic acids makes the deposit non-adherent. Tartaric and citric acid are not generally classed as reducing agents although the former does reduce silver from alkaline or even from neutral solutions. Any reducing action they might have would be negligible in the pres-

[8] Smith, Z. anorg. Chem., **4**, 237; through Trans. Am. Electrochem. Soc., **26**, 62.
[9] Fischer, Ber., **36**, 3346 (1903).
[10] Hughes and Withrow, Jour. Am. Chem. Soc., **32**, 1573.

ence of the free nitric acid. It seems that the effect of these acids cannot be due to their reducing properties.

Silver phosphate in phosphoric acid solution gave a spongy deposit.[11] Pyrophosphoric and nitric acid in silver solutions showed no advantage over cyanide for quantitative work.[12] No mention was found of the deposition of silver from solutions containing metaphosphoric acid.

No physical experiments were tried to determine the reasons for the beneficial action of the acids. Complexes between the silver, the tartaric acid and the iron, when present, might be the essential thing.

Addition agents in silver nitrate solutions only have been considered in this review and in this research.

SUMMARY.

Tartaric acid is the most effective substance for producing solid, firm deposits of silver from the ordinary silver refining bath containing silver nitrate and nitric acid. A good composition of the bath is 3 percent each of silver as silver nitrate, nitric acid and tartaric acid. The further addition of 0.01 percent of glue twice daily makes the deposit much smoother and of a darker, more shiny color.

The addition of 2 percent ferric nitrate to the above baths makes the deposits much smoother, darker and more shiny. Analysis of a cathode showed 0.086 percent of iron.

If economy in addition agents is desirable at the sacrifice of some smoothness in the deposit, 0.5 percent tartaric acid and 0.01 percent of glue twice daily can be used. More tartaric acid must be added after about 100 grams of silver have been deposited from each 100 cc. of solution, otherwise loosely adhering crystals are formed.

A current density of 22.4 amp. per sq. ft. (2.45 amp. per sq. dec.) in a vigorously stirred bath gave a firm, smooth deposit which was a little heavy on the edges. A current of 35 amp. per sq. ft. (3.8 per sq. dec.) gave a firm deposit with still rougher edges. In a bath only gently mixed or stirred, 7.4 amp. per sq. ft. (0.8 amp. per sq. dec.) gave the best results. With 6 percent

[11] Smith, Am. Chem. Jour., **12**, 335.
[12] Brand, Z. anal. Chem., **25**, 592.

silver solutions, 14.8 amp. per sq. ft. (1.6 per sq. dec.) could be employed.

The ordinary addition agents as glue and peptone, by themselves, only partly restrained the crystalline structure and did not produce smooth deposits.

Metaphosphoric acid caused the deposit to be hard and non-crystalline but the bath soon deteriorated.

The weight of tartaric acid used up is 0.005 of the weight of silver refined. The maximum cost of the tartaric acid and the glue at present prices is 0.23 cent per pound of refined silver.

The deposit is brittle, hence it is of no value in plating.

The authors wish to thank the American Electrochemical Society and its Committee on Assisted Research for the loan of the silver bullion which was used in this research.

Indiana University, Bloomington.

DISCUSSION.

President Addicks: There are really two points of view which can be taken in refining silver, one is the refining of silver by the commercial refiner and the other is the refining of silver by the Government. The latter is not particularly interested in the tied-up value, which is one of special concern in the private plant. From the commercial point of view I do not see where we have anything to gain from making an adherent deposit of silver. It is necessary to have a starting sheet of rolled silver, or its equivalent, which is melted up with the deposit. The ordinary custom is to use a graphite plate and a non-adherent deposit. A good deal of nitric acid was used in these baths, three percent, far above ordinary practice, and that is one reason why the addition agent was destroyed. The main thing is to turn the silver over very rapidly, and use high current density, but that means heating and requires less nitric acid to be used. We therefore run the bath warm, with as little free nitric acid as is necessary to make up for the depletion of the silver. We use enough nitric acid to have some chemical action, but it is a very small amount, something like 0.2 or 0.3 percent.

I hope we may hear something on this point from some of the gentlemen who are connected with the Government Mint.

F. P. DEWEY: We give very little attention to the question of producing an adherent deposit. It is of no value to us. While we are not at all interested in the tying up of the money in either the gold or silver cells, yet we do want to get the silver out of the way, and into the form of bars on our shelves. Therefore we work as rapidly as possible, and we would have practically no interest in making an adherent deposit.

G. B. HOGABOOM: It would be interesting to know how electrolytic silver would act as an anode in a silver bath. Electrolytic copper makes a better anode than either cast or rolled metal. One of the difficulties in silver plating is to get an anode that will remain white in a solution. A large manufacturer of anodes controls the market because he guarantees his product not to turn black in a solution. If a government bar is used as an anode, although its purity may be very high, it will turn black in a silver solution. Probably electrolytic silver would remain white in a solution.

F. A. LIDBURY: What is the nature of the black film?

G. B. HOGABOOM: An analysis showed presence of peroxide.

PRESIDENT ADDICKS: That would seem to locate the responsibility definitely on your own shoulders.

G. B. HOGABOOM: In what way?

PRESIDENT ADDICKS: It certainly is not in the bar when you receive it.

G. B. HOGABOOM: The condition cannot be controlled by the plater, but is controlled by the refiner, since anodes that remain white can be bought.

G. A. ROUSH: A thing that would require some attention before the electrolytic cathodes could be used directly as anodes in a plating bath is the presence in the cathodes of some of the addition agent. As shown in these analyses, the loss on ignition was as high as 1.8 percent, and on solution of the metal, this addition agent will be added to the plating bath, and while these agents are advantageous in a refining bath, they might not be in a commercial plating bath.

PRESIDENT ADDICKS: It is customary in melting cathode silver to add copper wire to bring the fineness down to what you are paid for, in some cases 999 and in some cases 998.5, but nothing in excess of these limits, what ever they might be; the refiner dilutes silver with copper to get more money out of it.

GEORGE W. VINAL: In working on the silver voltameter at the Bureau of Standards we have had a different point of view from that of the electroplater. The best deposit for us is the crystalline deposit, which we find to be much purer than the smooth deposit. It has been a matter of great importance to have this deposit as pure as possible, and one step in that direction has been to use very pure anodes.

We have found that the best anodes for the silver voltameter are those coated with electrolytic silver. The amounts of the impurity in this silver are probably of the order of a few thousandths of one percent.

As to the slime that is formed on them, I can say that the slime on the electrolytic silver is much less than it is on the rolled silver anode, and even in the case of silver as we have obtained it from the mint we have made a uniform practice of depositing silver on the anode before using it in the silver voltameter. As a general rule the slime on the anodes made of rolled silver such as we obtain from the mint is black, as Mr. Hogaboom has said, but the slime on the electrolytic silver is practically always gray, and much less in amount.

As to what this slime is, I think if you will refer to the literature on the silver voltameter you will find that there are as many guesses as to its composition as papers dealing with it. We have made some tests on it at the Bureau; so far as we are aware it is very finely divided silver and probably fairly pure.

F. P. DEWEY: I would ask Mr. Vinal if he refers to our electrolytically refined silver or to the proof silver, such as was analyzed by Dr. Allen.

GEORGE W. VINAL: We have asked for a silver of the highest grade from the mint. I do not think that the slime on it is any reflection on the mint. I think the question of slime is largely a question of surface hardness of the silver. Whenever silver which is rolled or cut is used as the anode it will flake off, accom-

panied by slime. The electrolytic silver is probably of more uniform hardness.

F. P. Dewey: My recollection is that we have supplied your department some of our electrolytic silver which runs 999.75 fine, sometimes 999.9, and I was interested in knowing whether you had used that, or whether you used the proof silver, such as you had from the Philadelphia mint, running somewhat higher than that in purity. A sample has been analyzed by Dr. Allen and the composition given in one of his papers.

George W. Vinal: The purity of the silver I referred to as containing only a few thousandths of one percent of impurity is the silver deposited on the cathode when we were measuring the international ampere. I completed a series of measurements on its purity last year, the results of which were published a month ago (J. Am. Chem. Soc., **38**, 496) and under our best conditions the impurities were found to be 0.004 percent, on the average.

F. P. Dewey: That would indicate it was electrolytic silver rather than our proof silver.

Joseph W. Richards: I regret very much that the Bureau of Standards uses the term "voltameter" in this connection, instead of coulometer.

George W. Vinal: The word "voltameter" certainly describes inaccurately what the instrument does. At the London Electrical Congress, in 1908, the question was considered and they decided to retain the word "voltameter" because of its derivation. The word was coined by Faraday in 1834. He applied the name to his instrument of volta-electrometer, and that was shortened afterwards to voltameter.

F. A. Wolff: We recommend that the word coulometer be substituted in place of the word voltameter.

A paper read before the New York Section of the American Electrochemical Society, in Joint Session with the American Institute of Electrical Engineers, March 10, 1916. Called up for further Discussion at the Twenty-ninth Meeting of the Society, in Washington, D. C., April 27-29, 1916.

CORROSION AND THE ENGINEER.

By W. H. Walker.

In the valuable contribution of Dr. McCullom and his co-workers at the Bureau of Standards upon the corrosion of iron structures when buried in the ground,[1] a terminology is employed which is very useful in discussing the damage occasioned by stray electric currents, as contrasted with that caused by the natural corrosion of the iron unaccelerated by an external electromotive force. But while it is logical to call the first type of corrosion "electrolytic," because induced by the flow of an impressed electric current, it is, however, illogical to describe the latter type as "self-corrosion" because of the unavoidable inference that it is not electrolytic, but is purely chemical in its nature. It may possibly be due to this lack of a clear conception of the mechanism of natural corrosion on the part of the electrical and mechanical engineers that is due to the fact that they have displayed so little interest in the subject, and have so tardily availed themselves of the knowledge of the phenomena now at their disposal.

In dealing with problems of corrosion the engineer is satisfied if he can explain a phenomenon by stating "that a galvanic cell is set up." Thus a piece of coal in contact with an iron plate or a bit of mill scale on a pipe will cause a pit to form "because it sets up a galvanic cell." From a chemical point of view both the coke and the mill scale are perfectly inert; how then can they cause galvanic action—what rôle do they play in the solution of the iron which produces the pit?

Eight years ago it was my privilege to present before this Society a paper[2] on the function of oxygen in the corrosion of iron in which I offered an explanation for the galvanic action of such inert bodies, and made some applications of the facts described

[1] Trans. Am. Electrochemical Soc. (1916), **29**, 469.

[2] Transactions, American Electrochemical Society (1908), **14**, 175.

to general engineering practice. Time has shown that the conclusions here drawn were correct. But obviously this paper was not so clearly written, nor were the facts so convincingly told as to attract the attention of the engineering fraternity to it, or at least to occasion any discussion of it. Engineering magazines continue to publish lengthy articles upon the pitting of boiler tubes, the rusting of water supply systems, the red-water plague, anti-corrosion compounds and the like. These papers describe the symptoms and generally prescribe a cure, but say never a word as to the cause of the trouble.

What would be thought of the medical profession, for example, if it continued to write only regarding the drugs to use in a case of typhoid fever but did not interest itself in the cause and its removal? As a matter of fact, this is an age of preventive medicine. We sterilize the water and inoculate the man in order to prevent the malady. Not so the engineer. He continues to drug his boiler or physic his hot-water-supply system in a vain attempt to cure the disease, but takes no steps to prevent it. He gives whiskey and quinine to help a neurasthenic, when luckily he cures a bad, but unsuspected case of chills and fever.

Within the last few months there was presented before our largest national engineering society by an electrical engineer a paper which contains data exceedingly important to the profession and which are none the less valuable because old. We gladly recommend this paper[3] to all who are interested in the corrosion of steam boilers, especially the truly novel portion which consists in recommending a constant observation of the water in the boiler itself, by the engineer in charge, and not simply a study of the feed water alone by some absent chemist. However, the paper would have been increased in value many fold if the author had studied his problem from the point of view of the cause of his trouble and showed the existent relationship between the cause and the cure. In fact when he essays to mention a cause he falls into grievous error. For example, he states: "But it is very evident that the low osmotic pressure of distilled water is the direct cause of the corrosion." Now of all the factors influencing corrosion osmotic pressure from whatever source is the least active —is in fact practically negligible.

[3] A novel method of handling boilers to prevent corrosion and scale. By Allen H. Babcock, Am. Soc. Mech. Eng., 1915.

Corrosion is an electrolytic phenomenon and can be understood by electrical engineers on purely electrochemical grounds. It takes place at ordinary temperatures only in the presence of water through the reaction.

$$Fe + 2H^{\cdot} \rightarrow Fe^{\cdot\cdot} + 2H$$

This means that a metallic iron atom electrically neutral interacts with two hydrogen ions present in the water and which carry electrical charges; the result is the production of an iron ion which takes up the two electrical charges from the hydrogen ions and the deposition of two atoms of hydrogen. Energy is lost to the surroundings and appears as electricity and heat.

The factors which influence the action are, first, the *solution pressure of the iron.* This is constant for all samples of iron under constant conditions, but may be influenced by a number of agents. Thus the immunity of iron to corrosion in solutions of chromic acid is undoubtedly caused by the passivity of the iron —a thing which, whatever its true nature, is equivalent to lowering the electrolytic solution pressure of the metal.

The impression of an external e. m. f. may also be considered as equivalent to a change in solution pressure. This may be either positive or negative in its direction. If the potential employed be mechanically generated, we speak of it as "stray currents," but if electrochemical in its origin, it is described as the accelerating or retarding effect of other bodies. Thus iron, which itself is incapable of corrosion when imbedded in concrete, is severely attacked if its solution pressure be sufficiently increased by having superimposed upon its own potential an external e. m. f. due to stray currents. On the other hand, the potential of iron may be so depressed by an impressed e. m. f. due, for example, to the solution pressure of zinc, that the iron in contact with zinc will not corrode.

Second, the *number of the hydrogen ions.* The greater the concentration, the more rapid will be the corrosive action. Hence, if any substance forming hydrogen, such as carbonic acid or bicarbonate or sulphur dioxide or any acid-forming compound, be present, corrosion is accelerated. On the other hand, if an alkaline material such as soda ash or caustic soda be present, the number of hydrogen ions is decreased and corrosion is retarded.

If enough hydroxyl (the active ion of an alkaline compound) be present, practically all of the hydrogen will disappear and corrosion will entirely cease.

In the paper on boiler corrosion already cited, the author has simply added another example to the many already existent, which proves that carbonate of soda in sufficient amount will prevent corrosion in the manner just stated. His suggestion that the engineer readily examine the water in his boiler by withdrawing a sample and titrating it with standard acid is a novel one, and highly to be recommended. Full directions for doing this are given in his paper.

Third, the *ease with which the hydrogen ion reaches the iron.* For example, the wonderful resistance of sheet steel containing small quantities of copper to corrosion when used as roofing is unquestionably due to the adherent nature of the film of oxide produced when corrosion starts. This film, as in the case of the aluminium oxide coat on metallic aluminium, effectually insulates the metal and practically prevents further corrosion.

Fourth, the *osmotic pressure of the iron ions.* This is so small in any case that it is negligible; in the presence of oxygen it is kept extremely low owing to the formation of insoluble iron hydroxide.

Fifth, the *deposition of the hydrogen and its removal by the depolarizing action of oxygen.* The accelerating action of metals such as platinum, copper, and lead, and materials such as coke and mill-scale upon the corrosion of iron are undoubtedly due alone to the aid these bodies offer to the elimination of the hydrogen produced by the corrosion reaction, owing both to the low overvoltage of hydrogen upon these substances and to the high catalytic action of these materials on the hydrogen-oxygen reaction by which the deposited hydrogen film is removed.

While in specific cases the corrosion of iron can be absolutely controlled by first one and then another of these factors influencing it, too little attention is generally paid to the last one. The retarding action of the hydrogen film which is stable in the absence of oxygen and any acid-forming compound is so controlling, that from this point of view, oxygen (or air) may be said to be the cause of corrosion. If oxygen be completely removed from boiler feed-water, the boilers will not pit or corrode.

If oxygen be separated from the feed of ordinary hot-water supply lines, the "red-water plague" and other corrosion troubles will disappear.

By this removal of the cause of the disease not only are all its ill effects avoided but the necessity of drugging with alkali, removal of the products of corrosion, and such curative measures, with their attendant evils, are eliminated, and in this as in so many other cases experience has proved prevention to be better than a cure. If electrical and mechanical engineers will only take more closely into their confidence their brother electrochemists, we can together more quickly make available the knowledge on the subject of corrosion already at our command for the elimination of the difficulties which corrosion introduces into commercial practice.

DISCUSSION.

(At New York, March 10, 1916).

W. K. Lewis: At the conclusion of the paper Prof. Lewis showed various ferroxyl indicator slides, among them one in which iron was connected with aluminum. He pointed out that aluminum fails to protect iron on account of an adherent coat of oxide on the aluminum, despite the high position of aluminum in the electromotive series. The fact that zinc, less electro-positive than aluminum, protects iron is proof of the absence of such an insulating oxide film on the zinc. The resistance of pure zinc to corrosion cannot, therefore, be due to an oxide coat but is caused by the high over-voltage of hydrogen on zinc and the low catalytic action of zinc on the depolarization of hydrogen by atmospheric oxidation.

A. S. Cushman: New theories are continually being advanced in the attempt to explain corrosion difficulties as well as to overcome them. Among some of these recent theories, it has been asserted by a group of collaborators in this country that the addition to, or the accidental presence in, iron or steel of a very small quantity of copper will make the metal resistant to corrosion. It is perhaps well known that I do not accept this theory on the

basis of any evidence which has so far been presented. Nevertheless, I am attempting to keep an open mind in regard to these claims, for if it can be shown that this theory is correct, we have an easy way of overcoming corrosion dangers and difficulties.

I have gradually been led to the conclusion that homogeneity, soundness and chemical purity of a metal are factors that have to be taken into account in determining whether a metal is more or less resistant to the various conditions of service. On the other hand, it has been repeatedly stated that all that is necessary to be done, if high-corrosion-resistance steel is desired, is to see to it that the metal shall contain, say, 0.04 of one percent of copper, although it is further alleged that 0.25 percent of copper is better. The only comment I wish to make on this theory at present is that if this claim is correct, it furnishes the basis of the easiest specification that has ever been offered to the engineering profession. We can change a batch of steel into coppered steel by throwing a couple of handfuls of pennies into the door of the open-hearth furnace, a process which tempts me to denominate it as a "penny-in-the-slot" proposition.

I have had hundreds of samples of full-sized sheets of varying analysis under my observation for a number of years. Over three hundred of these full-sized sheets, all of No. 26 gauge metal, have been out-of-doors for over three years. In setting out these tests, I and my associates took the greatest care to see that they were properly gauged, and, above all, that they were all of the same gauge. The sheets were not only measured with a micrometer but they were weighed individually to see that no great variations of thickness occurred. In making exposure corrosion tests, this is an important point which is often overlooked. If we are considering two pieces of metal under test side by side, of any given analysis, brand or make, and suppose one of them to be twice as thick as the other, it is generally found to be true that the one that is twice as thick as the other will not last merely twice as long: it will last much longer than twice as long. In fact, I think it would be safe to say that the ratio of longevity under any given conditions of atmospheric exposure would be more nearly in a geometrical ratio than in an arithmetical one. This is only one of the points that make it so difficult to reach fair conclusions from the results of incomplete exposure tests.

Among the hundreds of sheets which have been under my observation, most of them have been under exposure in a Western mill town surrounded by smoke stacks and chimneys, while others have been in the clearer, purer air of Washington, D. C. These test sheets have included ranges of copper all the way from traces up to 0.5 percent, while some exceptional sheets have as high a copper content as from 1.5 to 2.0 percent. I have cut from these large sheets which were exposed in Washington some small samples to present to this audience tonight. I think everyone who cares to examine them will agree with me that the effect of copper in producing an excellence of surface is not shown by these examples. A careful inspection of the whole lot of my full size sheets leads generally to the same conclusion. It is true that the Bessemer steels which usually contain very little copper rust more quickly than the general run of open-hearth steels. This, however, does not justify the conclusion that Bessemer steel rusts more quickly than open-hearth because it has low copper. This tendency of Bessemer steel to rust quickly, I think, can be satisfactorily explained from an entirely different point of view. It is a curious fact that in my tests that have been under atmospheric exposure for more than three years, having gone through three winters, exactly eight of the hundreds exposed have failed, and everyone of these, to the best of my knowledge, is Bessemer metal.

The principal gases which we have to consider as associating themselves with steel are oxygen, hydrogen, nitrogen, carbon monoxide, and to some extent carbon dioxide. It is not always clearly understood that gas can associate itself with metal in three separate and distinct ways:

First, it may exist in the metal in the condition of atmosphere, in blow-holes. All metallurgists are aware that it is very difficult to pour ingots of molten metal and have them entirely free from blow-holes. It is, of course, possible that if these internal blow-hole surfaces are not oxidized, they may weld up in the process of rolling or forging, but if this is the case we are unable to state whether this gas, that I have termed atmospheric, is still held in the metal or passes out of it.

Second, the gas may be occluded in the metal in the form of what is sometimes termed solid solution.

Third, the gas may be combined with the iron to form oxides, hydrides, nitrides, or carbonyl compounds.

I have recently been paying special attention to the gas content of various types of manufactured metal, and I have been particularly struck with the fact that in my corrosion tests both sheets which have failed as well as sheets which are showing signs of early failure all show high gas content, irrespective of whether they are copper-bearing or not. I have found as a rule that samples of steel which rust quickly usually show from five to ten times more gas content than those samples which are resistant to corrosion. In addition to this I have collected from every possible source as many samples as I could get that show unnatural or undue lack of resistance to corrosion under service conditions, and in every striking case which I have studied so far I have found high gas content accompanying a tendency to corrode rapidly. I have recently had occasion to study the corrosion of a pipe in service in a Western State, in which one section of the pipe-line corroded, whereas neighboring sections were still in good condition. Analysis showed that the pipe which was failing rapidly had a nitride nitrogen content of 0.041 percent, whereas the pipe still in good condition showed nitride nitrogen 0.004 percent. The copper content of both sections was comparatively low, and nothing is more certain than that the difference in resistance to corrosion under these service conditions was not attributable to any variation in the copper content. I have also studied an interesting case of some railroad spikes from a Western State, some of which rusted in a most remarkable manner in service. In this case, again, analysis showed the presence of an unduly high nitrogen content.

Maximilian Toch: My connection with corrosion of metals has been more practical of late years than theoretical, and in view of the fact that up to now no structural steel has been made which does not corrode, I have busied myself with making materials in the nature of paint or paint compounds which prevent progressive oxidation. I am frank to say that the news which Dr. Cushman has given out tonight concerning the manufacture of iron containing copper, which is non-corrosive, is very interesting; and at the same time, as soon as steel will be made which will be rust-

proof I will have to look around for something else to do, because there will be no need for paint.

The lantern slides of Mr. McCullom, showing briquettes in which steel had been embedded and a current passed through, remind me that ten years ago I made a similar research, with the absolute conclusion that the cathode steel never rusted and the anode steel always rusted, that neither of the two rusted when coated with an alkali-proof insulating paint, and that the anode could only rust if the pressure of the concrete was insufficient to prevent the reaction. It was stated that the experiments were conducted with iron and lead buried in soils, yet the paper does not indicate the strength or quality of the electrolyte in these soils, for in absolutely dry soils no corrosion could take place. In order to produce corrosion you must have both oxygen and water, and there is no indication of this in the paper.

When I made the investigations of the condition of the steel and metal of the battleship "Maine," when the hull was finally uncovered in 1912, evidences of electrolytic corrosion were manifest, and one particular picture of a bronze binnacle stand that was adjacent to a steel ventilator shaft showed that these two had coupled, the bronze being the cathode and the steel shaft the anode, with the result that the steel ventilator shaft was entirely eaten away and the bronze binnacle stand left in perfect condition. On the other hand, we know that cast iron or iron having a coating of silicide of iron is proof against corrosion, for the very pump that was used for emptying the hull of the battleship was the pump which had been subjected to salt water in the hold of that ship for thirteen years, and when it was taken out only a few connecting rods had to be replaced, the balance of the pump being in excellent condition.

Some years ago, Dr. Hering proposed before the American Electrochemical Society a method for bonding structural steel in buildings to prevent corrosion, by means of a zinc anode plate. I do not know whether this was ever tried out in practice, but theoretically it appears to be sound.

Steel or iron rusts progressively, but zinc and lead do not. In Belgium, roofs are protected with zinc plates, which turn white by reason of the fact that a very fine film of hydrated oxide of zinc is formed, and once this coating is formed no further corro-

sion takes place. I am working on this very interesting problem now, because iron or steel rusts progressively, which has led me to the conclusion that there may be anodic or cathodic forms of rust, and my belief, now, although I have not yet demonstrated it to my entire satisfaction, is that iron rust is cathodic and zinc and lead are anodic, which would indicate that the electrochemical influence of these hydrated oxides is such that iron continues to rust whereas lead and zinc become immune.

(In Washington, D. C., April 27, 1916).

G. A. Roush: If you send a rapidly alternating current between two electrodes one plate is instantaneously anode and some of the metal is dissolved, at the next instant this plate is cathode, and since it is surrounded by the solution containing the metal dissolved while anode, the metal is deposited, providing the reversal takes place before there is a sufficient time for appreciable diffusion. This replaces the metal on the same plate from which it was dissolved, leaving the plate only slightly affected.

As the length of time between reversals is increased, the proportionate losses at either plate increase until finally, at periods from one week to two weeks, depending on the various conditions, the diffusion is so great that a large proportion of the dissolved metal has been removed from the vicinity of the anode, and cannot be redeposited during the succeeding reversal, leaving a considerable net loss by corrosion. The net loss by corrosion is therefore proportional to the diffusion that can take place during the electrolysis and will increase with the time allowed for diffusion, and with increase in diffusibility in the materials surrounding the electrodes.

In previous discussion on the subject of corrosion, frequent mention has been made of the addition of copper to steel. The question of the use of copper to prevent corrosion of steel is generally accepted as being of recent origin—within the last ten years. The start along this line, however, seems to have been made as long ago as sixty years. In glancing through an "Encyclopaedia of Universal Knowledge," published about 1855 or 1856, I found a chapter on "The Preservation of Metals," in which the statement was made that iron could be made much less subject

to corrosion if it were melted in a crucible and a small proportion of copper added, the resulting alloy being more permanent than the original metal.

A. S. CUSHMAN: The suggestion that the addition of small quantities of copper to steel confers upon the steel extraordinary resistance to corrosion is by no means new. I have come across similar statements in old books on corrosion, and the idea has cropped up from time to time in the literature of the past fifty years. If increased corrosion resistance can indeed be conferred so simply and economically, it is worth knowing, but it is a curious thing that now that the attention of chemists has been called to this subject so frequently, it is found that almost all steels for years past have been carrying small quantities of copper. In fact, it is a very difficult thing to find a piece of steel that does not carry a little copper. Since this is so, why is it that we have had so much trouble with steel corroding rapidly? It has been stated recently that 0.04 percent of copper in steel will impart added corrosion resistance, and yet the steel plants of this country have been making steel with more copper than this, as a regular thing, owing to the fact that their ores, pig iron and other raw materials carried a definite copper content.

I would like to take this occasion to say that this meeting of the American Electrochemical Society has been of the greatest interest and benefit to me, as I am sure it has been to all other members. It is my belief that our opportunities for doing good are greater than ever before. I have become aware that there is an impression, especially among technically educated men, that our legislators in Congress are unfit and that they cannot properly discuss problems which involve highly technical information. It is my belief, however, that if we as technologists would make the effort to get together more with the gentlemen who represent us in Congress, it would be an action which would be sure to lead to good results. Our representatives in Congress are shrewd, capable men, and while it may be true that they do not know what we know and that we can teach them many things, it is none the less true that they know a great deal that we do not know and that we should endeavor to understand the so-called politician's point of view. I have found many Congressmen and Senators

earnestly endeavoring to instruct themselves on the modern technical problems of the day, but I have rarely met with a chemist or engineer that thought it worth his while to try to understand some of the problems that public men have to meet.

F. N. Speller: All who have to do with the design and maintenance of iron structures should be familiar with the facts governing corrosion so as to intelligently apply means to minimize this trouble. Our research laboratory has naturally been interested from the first in this problem so that what I have to say applies particularly to the conservation of pipe.

The majority of engineers and architects seems to think that it is up to the metallurgist to produce a metal which will withstand any condition of service. In a measure this is so; but for economic reasons we are at present obliged to use a weldable form of iron for most pipe. It is the nature of iron to corrode, and it is very doubtful if this natural tendency can be overcome without interfering with other essential properties and seriously increasing the cost of the product.

The development of steel pipe, in the past ten years, towards greater durability has probably added at least 50 percent to its life, without material increase in cost. Compared with this achievement, it has been proved that by removal of most of the free oxygen from water the life of iron pipe may be prolonged four or five times.

The importance of free oxygen as an agency in the destruction of water pipe was recognized and pointed out by us before the true function of oxygen was explained by the electrolytic theory of corrosion. Early observation of the action of water on piping systems showed that with the same kind of pipe and water and the same range of temperatures one system would last three or four years while another would show no deterioration to speak of after 25 years, depending on whether free oxygen was brought into the system or not.

With a knowledge of the fundamental cause and controlling factors it should be easy to control this trouble in most of our piping systems, as the amount of oxygen to be removed is comparatively small.

BRADLEY DEWEY: It would seem to me that the relationship between electrical and mechanical engineers and their brother electrochemists must become more and more like that of the mechanical engineer and the chemical engineer when working on combustion and boiler-scale problems. In the every day solution of these latter problems the chemical engineer has become but a silent partner. Working through the medium of technical literature and aided by the educational work carried out by manufacturers, he has given the mechanical engineering profession an understanding of the chemical principles involved and they in turn are making the applications. Is not the relationship between the electrochemist and the electrical and mechanical engineer much the same? Having now largely developed the fundamental laws of corrosion, the electrochemists must redouble their efforts to instruct their fellow engineers in these fundamental principles. In this campaign they will, of course, receive the greatest help from progressive manufacturers.

When once the term "galvanic action," and the expression "because it sets up a galvanic cell" are barred from the engineers' vocabulary the battle will be half won. Dr. Walker's presentation of the principles underlying corrosion should be of the greatest help in eliminating those undesirables. The engineer will intelligently apply preventative measures only when, in considering a corrosion problem, he thinks of (1) the solution pressure of the iron as influenced by pacifying agents and impressed electromotive forces, (2) the number and concentration of the hydrogen ions available, (3) the ease with which the hydrogen ions reach the iron, and (4) the speed at which the deposited hydrogen either passes off as gas or is removed by its union with oxygen.

Realizing the full significance of these factors he will appreciate that the prevention of atmospheric corrosion is to be largely brought about by rendering it difficult for hydrogen ions to reach the iron; the prevention of boiler corrosion, by cutting down the number of hydrogen ions and eliminating oxygen from the water, and the prevention of pipe corrosion, by eliminating impressed electromotive forces, minimizing the hydrogen ion concentration where possible, eliminating the scale which acts as a catalytic depolarizer, and eliminating the oxygen which acts as a chemical depolarizer. These same principles should help not only the yacht

designer but also the pump designer who often uses bronze and iron in contact and seldom makes any allowance for localized corrosion due to mechanical depolarization. When these more generally applicable principles have been established, it will be soon enough to take up in detail their application in connection with some of the occasional apparent exceptions, such as the severe pitting caused by some so-called alkaline waters.

N. K. CHANEY: May not the failure of the engineer to make more general use of the electrolytic formulæ for corrosion processes be due to the failure of the theory itself to "make good" from a practical standpoint? And is not this failure the fault of the electrochemist?

It would seem that such questions are very pertinent in view of the fact that the electrolytic hypothesis has as yet failed to show the growing usefulness which is properly demanded of so fundamental a generalization.

It may be true that the large and chaotic mass of facts and data is not for the greater part incompatible with the electrolytic theory. The point is that these facts are generally neither predicted, demanded or explained by it. One such confession of failure we have in Dr. Walker's own words upon another occasion, as follows:

"One of the conclusions reached by a consideration of the electrolytic theory which has proved misleading is that homogeneity in the material insures protection while heterogeneity leads to rapid attack. While this is a corollary which may be logically drawn from the electrolytic theory, and is doubtless in itself true, there are evidently other factors which superimpose themselves, producing a final effect contrary to that predicted."

What is the engineer to think of the value of a theory which on the testimony of a distinguished electrochemist leads to conconclusions contrary to fact?

It is not as though the above criticism were an isolated exception. The plain fact is that the electrolytic theory has led to the development of no useful ways of predicting anything about the actual comparative corrosion values of different irons except the empirical test of "wait and see."

But electrochemists and engineers are certainly entitled to better

returns than the electrolytic theory has produced up to the present time. What is the matter?

It is the writer's belief that the exponents of this theory have been led to over-emphasize a matter of secondary importance, *to wit,* the existence of electrochemical potential differences between various parts of the metal surface, to the comparative neglect of the controlling factors, namely, the depolarization properties of the metal surface with respect to hydrogen.

Dr. Walker and many others have assumed that the conclusion that "heterogeneity of material leads to rapid attack" is a "logical corollary of the electrolytic theory." The logic of this assumption is open to question. If a zinc area is coupled with a copper area the corrosion of the zinc area is much increased. If the zinc area is coupled with a mercury area the corrosion is not increased beyond what it would be if the zinc area were coupled with another zinc area of equal size. The copper and the mercury are both inert and take no place in the reaction beyond conditioning the rate of discharge of hydrogen. In other words it is the overvoltage and depolarizing characteristics of the metal areas and not the homogeneity of the surface which is vital.

The differentiation of anode and cathode areas is not essential to the electrolytic conception. These are secondary phenomena which may influence the rate of corrosion or not.

If one could prepare a perfectly uniform surface of metallic sodium, there is no reason to suppose that it would not displace hydrogen from water and discharge this hydrogen freely upon its own surface. Each particle of sodium surface can act *both* as anode for the solution of sodium ions and as cathode for the discharge of hydrogen, without departing from the electrolytic conception of the process.

The fact that in practice irregularities and differences in potential would arise between different parts of the surface is a wholly secondary development.

Similarly a perfectly uniform surface of iron would discharge everywhere upon itself a perfectly uniform film of hydrogen. Then the reaction would continue at a rate determined solely by the rate at which this film could be discharged or oxidized.

Surface potential irregularities are not logically necessary to the removal of this film, though they would naturally arise where the surface is heterogeneous.

It is quite possible to postulate a perfectly homogeneous iron surface which would facilitate the removal of the hydrogen, or catalyze its reaction with oxygen, and so have a high corrosion rate, whereas the cathode areas of a heterogeneous surface might have high overvoltage characteristics, or stabilize the hydrogen layer and retard its reaction rate with oxygen.

In other words, electrolytic theory postulates as the sole criterion of the rate at which hydrogen can be removed from the surface of the metal.

The rate of this hydrogen removal or depolarization depends primarily upon the absolute solution pressures of the surface constituents and their overvoltage and catalytic properties, and only secondarily upon the relative potential differences between various parts of the surface.

A study of the characteristics of various iron surfaces from the standpoint of hydrogen depolarization will lead us into some very intricate physicochemical relations for which special technical methods may be necessary.

Such a study will lead us to an investigation of the rates and equilibria of the following possible reactions as determined by the specific dissociating, adsorptive, or stabilizing influence of various chemical constituents and physical conditions. As for example—

(1) 2H (monatomic) $= H_2$ (molecular) $=$

(2) $2O \rightleftharpoons O_2$

(3) $2H + O \rightarrow H_2O$

(4) $2H_2 + O_2 \rightarrow 2H_2O$

Attacks upon such problems as these will bring us to a real knowledge of the controlling and vital factors, and enable us to offer the engineer a working hypothesis instead of an academic theory.

A paper read before the New York Section of the American Electrochemical Society, in Joint Session with the American Institute of Electrical Engineers, in New York City, March 10, 1916. Called up for discussion at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

THE EFFECT OF RUST UPON THE CORROSION OF IRON AND STEEL.

By James Aston.

Such differences of opinion as exist regarding the mechanism of the corrosion of iron and steel are largely concerned with the more technical details, particularly the inception of rusting. The adherents of the acid theory contend that pure iron will not rust in pure water in the absence of an acid which exerts a direct solvent action upon the iron, together with oxygen to subsequently convert the dissolved iron into the familiar hydrated condition known as rust. Because of the abundance of carbon dioxide in the atmosphere, and its prevalence in natural waters through absorption, carbonic acid is usually the one upon which the defense of the acid theory is built, with a course of reactions as follows:

$$2\,Fe + 2\,H_2O + 2\,CO_2 \rightarrow 2\,FeCO_3 + 2\,H_2$$
$$2\,FeCO_3 + 3\,H_2O + O \rightarrow 2\,Fe(OH)_3 + 2\,CO_2$$
$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

These reactions require three molecules of water and three atoms of oxygen to convert two atoms of iron to the condition of ferric hydroxide. Furthermore, and this is the chief bulwark of the acid theory, there is regeneration of the carbonic acid, so that an infinitesimal quantity of carbon dioxide may rationally account for an infinite quantity of rust, if oxygen is available to assist according to the reactions cited above.

The electrolytic theory is based upon well understood principles. Given two electrodes immersed in an electrolyte, and forming a closed circuit by metallic connection external to the cell proper, there will be solution of the anodic electrode in quantitative amount proportional to its electrochemical equivalent as expressed by Faraday's Law. If iron is the anodic material, it will go into

solution at the rate of one gram per 3448 coulombs of current flow; or an equivalent of about 20 pounds (9.1 kg.) per ampere-year, equal to the metal in a plate one foot (30 cm.) square by one-half inch (1.3 cm.) in thickness. Each milliampere per square inch (6.3 sq. cm.) will represent a corrosion of 0.072 inches (1.9 mm.) of thickness per year; at this current density a 28-guage sheet will go into solution in approximately three months. Once the solution of the iron has been effected, there will be progressive oxidation to ferrous hydroxide and finally to ferric hydroxide, necessitating, for each two atoms of iron, three molecules of water and three atoms of oxygen to complete the reaction. Quantitatively, therefore, these relations are the same as indicated for the acid theory.

To state the reactions more nearly in accord with the mechanism of the electrolytic rust cell, solution of a single atom of iron at the anode means a deposition of its electrochemical equivalent, three atoms of hydrogen, at the cathode surface. Two atoms of iron will require six molecules of hydroxyl to oxidize it to rust, which is precipitated upon the anode surface; the six atoms of liberated hydrogen will in turn unite with three atoms of oxygen, and return to the electrolyte as three molecules of water. The net requirement is three molecules of water and three atoms of oxygen for each two molecules of ferric hydroxide formed. Oxygen is necessary to destroy the hydrogen film upon the cathode surface, thus effecting depolarization of the cell and insuring continuity of electrolytic action.

Based upon its broadest conception, it is universally admitted that solution may proceed by electrolytic action. Again it is not improbable that all solution of the iron is accompanied by liberation of electrical energy and flow of current in the quantitative amount indicated by Faraday's Law. The controversy hinges largely upon the contention of adherents of the electrolytic theory that pure iron is soluble to a slight degree in pure water, in the absence of carbon dioxide, and that in addition to water, oxygen alone is necessary to promote continuous formation of rust, provided conditions are such as to insure continuity of current flow. That usual conditions of corrosion involve lack of purity of the water, due to carbonic acid or equivalent matter in solution, and heterogeneity of iron, singly or collectively, is beyond dispute.

The essential factors for continuous electrolytic action are:

(1) Two dissimilar electrodes, both of which are conductors of electricity.

(2) An electrolyte in contact with both of the electrodes.

(3) A metallic connection external to the cell proper.

(4) A depolarizer.

With all factors present, electrolysis must go on; it will stop if any one is removed. Under usual conditions, iron exposed to atmospheric influences will tend to corrode because of the presence of all of the essentials for electrolysis. Heterogeneity of the exposed iron surface may be sufficient to set up potential differences between contiguous areas; this heterogeneity may be the result of various contributing causes. Moisture covering the surface furnishes the needed electrolyte; it is made more actively conducting by absorption of carbon dioxide, sulphurous, or other gases from the air, or by the various salts which may be in solution in water supplies. The interior portions of the iron give a metallic connection away from contact with the electrolyte. Oxygen of the air is a depolarizing agent for the hydrogen liberated by solution of the anodic iron and its subsequent oxidation to the familiar form of rust.

Electrode relations form one of the most interesting and important phases of the corrosion problem, and are the essential feature of this communication. Since lack of homogeneity is essential to establish differences of potential, it is but natural that constituents whose alloying relations with iron are those of chemical heterogeneity, should have attracted the principal attention of investigators. And since most of the impurities which exist in commercial grades of iron and steel are electronegative to iron, and therefore might readily promote its anodic solution, it was not unnatural to charge these inclusions with the greater part of the corrosion loss. But it is not logical to assume that chemical heterogeneity is the sole cause of potential differences, or that it is the most important contributing factor. For example, iron of highest purity may have adjacent zones strained to different degrees, resulting in potential differences sufficient to promote rapid disintegration of the more highly strained areas.

One factor that has not received the attention which seems

warranted is the influence of rust once formed upon the progression of rusting. Whether we fall back upon the acid or electrolytic theory to account for the inception of rust, we grant that it will form; for formation under the most unfavorable conditions is what each faction claims to prove. Once formed, what part does it play in subsequent reactions? Most authorities and publications rather briefly allude to the accelerating influence of rust, either by retaining moisture for longer periods, and thus prolonging electrolytic action, or because it is electronegative to the iron, and thus acts as a cathode in the galvanic couple. Lewes (*Trans. Inst. Naval Arch.*, 1887) ranks magnetic oxide (112), hydrated ferric oxide (65), and hydrated ferrous oxide (25), as electronegative to iron in the order and magnitudes given. Schleicher and Schultz (*Stahl u. Eisen,* 1908) have noted that a rusty plate is cathodic to iron, although their use of terms is rather confusing, and the opposite opinion might be gained from casual reading of the article. Heyn, in Germany, and Speller, in this country, have for some time consistently taken the stand that rust is a factor which in time overshadows differences in the chemical nature of the iron or steel, and thus becomes predominant in the progression of corrosion under usual conditions of service. Its influence is attributed to an electronegative potential.

As a result of much observation and study of the characteristics of rust, the following conclusions are advanced:

(1) Rust plays a rôle in the electrochemical relations at least equal to that of constituents usually assumed to be highly detrimental.

(2) Very probably in all cases, but almost certainly when rust is freshly formed, its influence is not as an electrode, but as a coating which affects the polarity of the underlying iron.

(3) Rust plays a dual rôle; the underlying iron may be anodic or cathodic to bare iron, depending upon the state of hydration. But fresh wet rust makes this iron electropositive.

(4) Rust is an accelerator of further rusting.

Taking up the above points in order:

(1) Magnitude of the Effect.

The relative magnitudes of electrochemical effect with various couples are given in the following tables:

Current in Cells—Milliamperes.

Anode	Cathode	1 Minute	Minimum	Maximum	Final
Zinc	Carbon	6.0			
Zinc	Copper	7.8			
Zinc	Iron	3.9 4.4	2.2–24 hrs.	3.9–3 hrs.	Thin rust on iron face.
Iron	Carbon	1.10 2.3 1.3 0.85	0.70–10 min.	2.70–24 hrs.	Anode even coat on face except where air bubble streak.
Iron	Copper	1.02 1.6 1.0 0.9	0.81–30 min.	2.7–24 hrs.	Steady rise—even green on iron face.
Iron	Mill Scale	0.43 0.35 0.40 0.25 0.15	0.25–1 hr.	1.40–44 hrs.	Bare iron, even rust on face.
Cold Rolled Steel	Iron	0.12 1.40 0.65	0.10–21 hrs.	1.1–4½ hrs.	In 21 hours, cold rolled even rust on face—iron patchy on face.
Wet Rust	Iron	1.5	1.21–15 min.	1.9–48 hrs. 2.1–91 hrs. 1.9–98 hrs.	1.8–120 hours. Iron clear on face, heavy patchy on back. Anode fresh wet rust, newly formed.
		0.91	0.91–1 min.	1.5–7 hrs.	1.15–24 hrs. Some original bare spots on anode now coated. Bare is clear on face, except few spots.
		2.0	0.80–24 hrs.	2.0–1 min.	Gradual fall to end—bare has spotted face—very heavy patchy back.
		1.5	0.55–24 hrs.	1.55–4 hrs.	Gradual fall after 4 hrs. Bare ⅓ patchy green on face.

Current in Cells—Milliamperes.

Anode	Cathode	1 Minute	Minimum	Maximum	Final
Iron	Dry Rust	2.0	0.61–30 min.	1.06–18 hrs.	No reversal in 18 hours. Rusty was thin yellow, air dried several weeks. At end, bare has even rust on face.
		1.6	0.65–1¾ hr.	2.0–1 min.	0.95–24 hrs. No reversal. Rusty was air formed and dried, thin even yellow.
		1.32	0–35 min.	0.66–8 hrs.	0.42–42 hrs. Reversed to rusty anodic at 35 min. and remained to end.
Wet Rust	Wet Rust	0.1	0.1–1 min.	0.42–73 hrs.	0.27–236 hrs. Both electrodes heavily coated at end. Cathodic has patchy formation. No reversal.
		0.85	0.11–24 hrs.	0.85–1 min.	Steady fall, no reversal. Both fresh rust, anode more even.
		0.10	0.07–4 min.	0.25–24 hrs.	Steady. Both fresh rust.
Dry Rust	Dry Rust	zero		0.30–8 min.	0.20–24 hrs. Reversal in 1 minute.
(A)	(C)	0.4	zero at ½ and 20 min.	0.50–1½ hr.	0.10–24 hours. Two reversals. (C) anode from ½ to 20 minutes.
		1.6	0.23–48 hrs.	1.8–2 min.	Steady fall.
Wet Rust	Dry Rust	1.2	0.68–15 min.	1.2–1 min. 1.16–5 hrs.	0.96–47 hrs. Anode fresh rust. Cathode heavy yellow.
		3.1	1.2–18 hrs.	3.1–1 min.	1.7–90 hrs. Anode fresh rust. Cathode yellow dry. At 18 hours both anodic to bare. Dry, 0.62 to 0.48 (5 min.); Wet, 1.30 to 1.07 (5 min.)
		4.0	0.6–46 hrs.	4.0–1 min.	Wet rust in water for several weeks. Dry is heavy yellow.

The readings are milliamperes of current flow in a cell with electrodes of 3 by 3 inches (7.5 cm. sq.) immersion, and ¼ inch (0.6 cm.) separation. Pittsburgh tap water formed the electrolyte, and to provide against slowing of the reactions due to exhaustion of oxygen, a gentle bubbling of air was maintained in the cell. Current readings were taken in preference to potentials, since they are a direct index of anode solution, and a flow of current in the circuit on the order of magnitude of that probably occurring in natural corrosion, should be accompanied to a great degree by the same secondary effects, polarization and the like, which are of importance in normal rust formation. Potential measurements with a high resistance voltmeter tend to cut the current to a small part of that which would occur in the short-circuited rust cell, with equal electromotive forces; while open circuit potential readings, however great, are no criterion of probable corrosive effect, since electrode resistance may decrease the effective current to a negligible amount. The internal resistance of the cell used in these tests was approximately 50 ohms, and that of the milliammeter 3.4 ohms.

The tables include only the significant data obtained in many tests, usually of 24 hours duration. Immersion variables are disregarded by citing the currents after a one minute interval. Maximum and minimum readings indicate the trend of current with lapse of time. Wherever possible or important, sheet iron electrodes of the same stock were cleaned and brightened, and tested for polarity. The currents were usually from 0 to 0.3 milliamperes, and were the result of surface preparation rather than quality of material, since more careful pickling and brightening would usually reduce, and often reverse, initial polarities. Whatever potential difference there might be in the bare electrodes, was made to act counter to the expected effect; for example, an anodic effect observed by coating one electrode with ferric hydroxide, mucilage, etc., was obtained only after overcoming the initial counter effect of the electrode material. As a measure of solution effect a current of 1 milliampere on the size of electrodes used, is equivalent to solution of 0.008 inches (0.2 mm.) of thickness per year, assuming maximum efficiency. This is a rate comparable to ordinary weathering action.

It is of interest to note that wet rust is anodic (1 to 2 m. amp.)

to bare iron, and dry rust is cathodic. The current densities are comparable to those of the iron-carbon or iron-copper couples. By wet rust is meant an electrode which has been in water a sufficient time to insure thorough soaking of the coating; while in the above tabulation the rust has, in addition, been formed in water and has never had an opportunity to dry out. Dry rust includes electrodes on which the rusty coating has dried out in air before immersion in the cell. For comparison, the zinc-carbon, zinc-copper, and zinc-iron values are noted, 6.0, 7.8, and 3.9 to 4.4 m. amp. respectively.

The anodic effect of the wet rust is also indicated in the zinc-iron, iron-carbon, and iron-copper combinations. In the former, local rusting of the iron caused the initial current of 3.9 milliamperes to drop to 2.2 at the end of the 24 hour period. In the iron-carbon cell, rust formed upon the iron electrode and increased its anodic effect from a low point of 0.70 milliamperes to 2.70 in 24 hours; while for the iron-copper couple, the increase was from 0.81 to 2.7.

Effect of strain is indicated by the electropositive relation of cold-rolled stock to ordinary iron, varying from 0.12 to 1.4 milliamperes. In the long period test this initial anodic effect was a minimum, but was nevertheless sufficient to cause rusting of the cold-rolled sheet, which rust in turn raised the current flow to 1.10 milliamperes in 4½ hours; the subsequent falling off to 0.10 milliamperes in 21 hours was due to patchy local rusting of the cathode, which cut down the effective cathode surface and introduced a counter electromotive force opposing that of the original anode.

The electronegative relation of black oxide scale in combination with bare iron was from 0.15 to 0.43 milliamperes initial current flow. Rusting started on the bare iron by this electrolytic effect, increased the final current to 1.40 milliamperes at the end of a 44 hour period.

For dry rust against bare iron, the effects are somewhat conflicting. Thorough wetting of the rust tends to lower its cathodic polarity with respect to the iron, usually to the extent of reversal. If however, the time needed is comparatively long, the rust produced on the bare iron surface may be sufficient to hold up the

anodic current without allowing reversal to take place. This same tendency prevails in the wet rust-dry rust combinations.

It will be noted that even though both electrodes are coated with rust of similar character, either wet against wet, or dry against dry, there are sufficient differences in amount or characteristics of the rust to cause current flow of appreciable magnitude; usually, however, with fall of current to relatively small amount after a considerable period of time, and often with reversals during the period.

(2) Nature of the Influence of Rust.

There is every evidence that the effect of rust, wet rust at any rate, is not as an electrode, but as a mechanical covering which influences the polarity of the underlying iron. These evidences are:

(*a*) The conductivity of wet ferric hydroxide is in no wise comparable to that of a metallic conductor; in fact it is much less than that of ordinary electrolytes. Measurements have given the resistance as 1000 ohms per centimeter cube; that of the tap water was 4000 ohms, while usual electrolytes will vary from about 1 to 100 ohms per centimeter cube, according to nature and concentration. The specific resistance of iron, on the other hand, is about 0.000012 ohm per centimeter cube.

(*b*) If metallic electrodes are brought closer together in the cell, the current will increase as the resistance of the circuit through the electrolyte becomes less; but actual contact of the electrodes within the cell proper will cause short circuiting, and consequent drop of the current to zero. With rusted electrodes, on the contrary, contact results in maximum current, and this increases still more with pressure. The effect is the same as the interposition of wet cloth, filter paper, or blotting paper between two metals.

(*c*) The anodic effect observed with wet rust may be obtained with numerous other substances, giving comparable and often even greater currents, and some of which cannot be other than inert as electrodes. Among these are precipitated iron hydroxide, rouge, manganese hydroxide, aluminum hydroxide, copper hydroxide, infusorial earth, gelatine, mucilage, parchment, and filter

paper. In fact, it is not unlikely that many materials of a colloidal or semi-permeable nature will have similar effect.

The underlying feature appears to be the relative access of oxygen to the surfaces of the electrodes. The electrolyte (moisture) must reach both; then that to which oxygen has the more free access becomes the cathode, and the other is the anode. If two bare iron electrodes are separated by a partition of porous earthenware, parchment, etc., either may be made the cathode by bubbling air into this compartment, and not into the other. Or by merely lifting one into the air and then reimmersing it. Dipping either electrode into hydrogen peroxide before immersing in the cell, makes it the cathode; with passivifying agents, as nitric or chromic acids, the effect is very pronounced. On the contrary, a pyrogallic acid dip results in an anodic electrode.

Wet rust or similar coating upon one electrode plays the rôle of a diaphragm permeable to the moisture, but preventing or slowing down the oxygen penetration. Anodic solution of the underlying iron results, with oxidation and precipitation as greenish ferrous hydroxide. This colloid, migrating outwards under the directive influence of the current flow, is in turn oxidized to ferric hydroxide nearer to the exposed surface of the rusted anode. The effect of rust and oxygen is well illustrated by local rusting of an iron sheet which has air bubbling up one strip or zone. Contrary to general expectation, this air supplied zone remains clear, while the adjoining areas are anodic and become coated.

Ferroxyl tests confirm the potential relations noted in the cells. The gelatine over iron plates upon which are spots of wet rust, aluminum hydroxide, parchment, and the like, is colored deep blue over the spots, and red at the surrounding bare areas. The ferroxyl test, also, indicates the importance of oxygen access in determining polarity. A sheet of iron will show red cathodic areas where oxygen penetration is quicker because of proximity to gelatine surface, holes cut in the gelatine, or holes cut through a parchment cover; while the covered areas, or where oxygen access is more difficult, will become the blue anodic zones. It is entirely likely that considerable misinterpretation of the ferroxyl tests has been made in the past because of failure to recognize the influence of the oxygen penetration or the excluding effect of rust or like surface conditions.

(3) Reversal of Polarity of Rust.

One of the confusing features of the investigation is the reversal of polarity of a rusty electrode after it has dried out. The mechanism of the transition is under investigation, and there is reason to hope for a solution of the problem. It appears above question that iron coated with freshly-formed rust which has had no chance to dry, is always anodic to the bare metal. Often there is diminution of current, and at times a reversal, but these effects may be satisfactorily accounted for by the unpreventable local action on the relatively large electrode surfaces. In fact, it may be stated almost as an axiom that the more the cathode face remains free from rust, the more the anodic current due to the rusty electrode will hold up to normal values. Also that when the anodic-cathodic areas due to alternate rusty and clear spots are brought within what one might consider as the zone of influence under the prevailing conditions of conductivity of electrolyte, etc., the rusty areas will automatically tend to sustain correspondingly clear zones while under water. Anodic rusting is even, whereas local action gives a patchy formation, due to alternate anode and cathode areas; and this formation is always greater on the uninfluenced back surface of the cathode sheet.

On the other hand, dry rust tends to reverse its initial cathodic characteristics, and to behave like fresh wet rust after varying periods of immersion. Seemingly this is accomplished equally as well by simple soaking in water as by the action in an electrolytic cell. The time for reversal varies with the character of the rust; that is the amount, its physical characteristics, nature of formation, drying, and the like. Also, when in a cell with bare iron, there is the probability of non-reversal because the initial cathode effect of the dry rust results in a sufficient coating of fresh rust on the bare electrode to counteract the tendency for reversal. In the mass of data accumulated, no definite conclusions can as yet be drawn. Reversals have been noted in a minute or less, and often in an interval from five to ten or fifteen minutes; usually the rust was rather spongy, and not old, and had not become very much dehydrated. On the other hand, it has often taken hours to effect the transition, and in numerous instances this has not resulted in 24 hours or longer period. Very generally, after a

moderate period without apparent reversal, the rusty electrode becomes the anode in a cell with a newly cleaned bare iron sheet; but this is not always true, and the anodic polarity does not appear to hold up as well as with rust which has not dried out. Well dried, closely adherent rust appears to hold its cathodic polarity most tenaciously; and it is more noticeable in the case of rust formed by long exposure to weathering or gaseous conditions of formation and drying, and where the coating has become hard, relatively impervious, and of dark brown color.

The reversal of polarity after wet rust has dried out, is probably due to various contributing factors; possible causes are:

(*a*) Change in degree of hydration. Since fresh wet rust closely resembles ferric hydroxide, and in drying out passes through several definite mineralogical forms of lower degrees of hydration, even perhaps to final approach to ferric oxide, it was but natural to assume that the change might occur during the dehydration period. Tests have shown that there is no measurable reversal of current during drying; it drops to zero and remains there. The reversal is on immersion after further drying. In one instance an anodic, wet rusty electrode was still electropositive to bare iron after fifteen and thirty minute intervals of air drying, whereas after one hour of drying it was cathodic, but reversed in five minutes. And yet after a forty-five minute drying period, there was no reversal of electronegative polarity in a test of 19 hours' duration. Other tests indicate that dried-out coatings of precipitated ferric hydroxide or of calcined rouge (ferric oxide) are either almost instantly anodic, or reverse much more rapidly than rust.

(*b*) Absorption of gases from the air—oxygen, nitrogen, carbon dioxide, etc. It is entirely likely that in drying, rust absorbs gases from the atmosphere, and these, oxygen in particular, may promote the cathodic effect. In support of this, anodic wet rust becomes cathodic on dipping in hydrogen peroxide solution. On the other hand, immersion of dried rust in pyrogallic acid did not result in a polarity change, nor in any definite decrease of the cathodic tendency of dried rust. Drying in vacuum was without appreciable effect, except a possible shortening of the reversal interval.

(*c*) There may be formation of an oxide or other compound of iron, in contact with the metal surface, which has electronegative characteristics of the metallic electrode type. Ferrous and magnetic oxides of iron play this rôle, and an analogous product may result to varying degrees with varying conditions of formation and drying.

The polarity characteristics of rust are worthy of careful study.

(4) Rust is an Accelerator of Further Rusting.

Since rust promotes electrolytic effects equal to or surpassing those of factors generally recognized as of marked importance, its influence in accelerating further rusting must be conceded. The reversal of polarity does not nullify the effect; where drying out occurs, there is a tendency for greater distribution of the rusting effect, while non-reversal of wet rust aids in intensifying the corrosion in concentrated zones.

APPLICATION OF PRINCIPLES.

Being one of the causes underlying the progression of rusting, the principles set forth in the preceding argument have a bearing upon the entire problem of corrosion. They have particular application to certain important phenomena.

There can be no denial of the principle that the effect of chemical heterogeneity becomes less with closer approach to purity in iron, and that one factor tending to promote electrochemical activity is diminished. Further, greater chemical homogeneity may promote physical uniformity as well. But does this accelerating influence extend beyond the mere inception of rust formation, and pass more and more into the background with lapse of time? May not the growth and spread of rust soon overshadow or obscure the relatively minute internal electrode aggregates and become the predominant factor in the subsequent rusting? Mill scale is definitely electronegative to iron; but by covering it with ferric hydroxide this electrode may be made anodic to the other one of bare iron. And if this is true, can we concede that purity of iron represents the solution of the corrosion problem; will we not come more nearly to accomplishment by having mechanical

barriers within the iron to obstruct the progress of corrosion, or by some alloy characteristics by which barriers are automatically produced or solution of the iron is checked?

Manganese sulphide has for long been the focus of particular attention. Tentative tests lend support to the statement of Cobb (*Jour. I. & St. Inst.*, 1, 1911) that manganese sulphide is virtually a non-conductor of electric current; therefore it can hardly be given much prominence as a cathodic electrode. Yet decomposition of manganese sulphide by natural weathering action may result in formation of manganese hydroxide and sulphurous acid; both may accelerate corrosion, the former in a manner analogous to wet rust, and the latter by increasing the conductivity of the electrolyte.

In fact, it is conceivable that an electropositive constituent of the steel, and ostensibly therefore a protector, may promote corrosion, since the anodic solution of this constituent may result in a colloidal product which will create an anodic zone in the underlying iron. Paint pigments, after weathering has destroyed the excluding effect of a poor vehicle, may accelerate corrosion of the iron because of a semi-permeable character.

All rusting proceeds by pitting, because of a series of alternate anodic zones, where solution occurs, adjoining similar cathodic surfaces, which are immune. Corrosion in the atmosphere is, however, usually more even and with less pronounced pitting, than in under-water or pipe service. In ordinary weathering, relative paucity of electrolyte and abundance of oxygen probably concentrate the zone of influence of the electrolytic effect. In addition, wetting of a dried rusted surface converts the rusted areas into cathodes and adjoining bare spots into anodes, and spreads the rust over the entire surface. The more frequent the alternate wetting and drying, the more even is the rust distribution. Investigation shows that these alternate reversals of polarity with periodic wetting and drying, set up current densities of very appreciable magnitude, even though the entire surface of the metal is apparently heavily covered with rust.

It is usual to ascribe pits to the presence of electronegative impurities associated with the iron. Pitting is likely to be most

pronounced in steel which is continually wet by immersion, and yet where there is the needed supply of oxygen. That inclusions in the iron may start localized corrosion and pitting cannot be denied; that they are other than a minor contributing factor is open to question. Lodgement of rust, sediment, organic matter, etc., or initial formation of rust by purely physical differences of surface condition, appear to be the general causes. Once rust has been formed, it will automatically promote anodic solution of the underlying iron, and will equally automatically tend to keep the surrounding cathodic metal free from rust. So long as the rust remains wet, there will be concentration of the corrosion in the restricted zone, with the well-known result of pitting. Naturally there will be some tendency for spread of the pitted area, due to greatly increased volume and spread of the rust. Experiments have shown that pure iron may be pitted by inoculating the surface with spots of ferric hydroxide, aluminum hydroxide, parchment, and the like, and exposing the plates in shallow running water. It is an often observed fact that rust formation, especially in water, has no relation to identifiable impurities in the iron, and is in greater aggregates than such constituents could possibly be. As a matter of fact, extensive study leads to the conclusion that the distribution of the initial rust is largely accidental; it is especially influenced by flow of water, which deposits rust or other matter in streaks in the direction of flow. The greater the tendency to cover up certain zones, and the greater the zone of electrolytic influence as affected by character of electrolyte, oxygen, and the like, the greater are the corresponding clear cathode areas. Pronounced pitting is a natural accompaniment.

To the contrary, in still water there is greater probability of even settlement of any matter, and less likelihood of disturbance of newly formed rust. There is thus a greater tendency for more numerous and evenly distributed small pits.

Water pipe service is usually severe. Constant flow of water carries rust or colloidal matter to a place of lodgement, and in addition renews the oxygen supply. Of vital importance, also, is the anodic relation of exposed iron to the heavy mill scale formed at welding heats. Rust formation is promoted, it covers the exposed iron, and augmented anodic solution of the rust-covered metal results. If, as is popularly assumed, rust is electro-

negative to iron, its formation upon the exposed iron surface should slow down the reaction, by covering an anodic area, and substituting for it a cathodic substance which is surrounded by the electronegative scale.

Bureau of Mines, Pittsburgh, Pa.
March 6, 1916.

DISCUSSION.

A. S. Cushman: It is perhaps well known that I have been interested in the subject of corrosion for many years. I am impressed more and more, as time goes on, with the complexity of the problem. Most certainly the corrosion of all metals is an electrochemical phenomenon in which electrolysis is a prime factor. There are, however, so many other factors that modify and affect the general result that sometimes, in spite of all the knowledge that has been gained on this subject during the last ten years, it seems almost impossible to account for the results observed.

When I began studying the corrosion of iron, a number of years ago, I looked upon it as a purely chemical problem. It was about 1906, I think, that I first ran across Dr. W. R. Whitney's suggestion, published in a brief note in the Journal of the American Chemical Society, that the corrosion of iron might possibly be linked up with Nernst's conception of the origin of the electromotive forces which are observed when certain chemical reactions take place. My mind once turned to this possibility, and I very soon convinced myself that the corrosion of metals was fundamentally an electrolytic phenomenon. In the early days of my researches on this subject, I made the discovery that if a perfectly clean polished surface of steel was immersed in water or in a salt solution containing a little phenolphthalein indicator, almost immediately pink spots or zones appeared upon

the surface of the submerged metal. This was a visual demonstration of the fact that hydroxyl ions were appearing at certain places on the surface of the steel and that electrolytic action was at work. A great number of these phenolphthalein tests were made, with similar results in each case. This discovery was talked over with Dr. W. H. Walker, who was also engaged upon a research on the same subject. As a result of our discussions the ferroxyl indicator was developed, Dr. Walker, as I recall, having suggested the addition of the reagent of ferro-cyanide to indicate the positive poles in blue, at the same time that my phenolphthalein reagent was indicating the negative zones in red. It was also Dr. Walker who suggested putting gelatin or agar into the reagent in order to prevent convection currents and permit the action to go on under observation for a longer time. To this combined indicator I gave the name ferroxyl. In our earlier publications, both Dr. Walker and I independently stated and restated the electrolytic theory by which the corrosion of metals was so largely explained.

I find myself in accord with much that has been said on this subject here tonight. I recall that Mr. Speller and I talked together, after my original publications on the corrosion of iron some years ago, on an important corrolary of the electrolytic theory, that is to say, on the importance of eliminating oxygen from pipe-line systems which are liable to internal corrosion. Mr. Speller has been making a special study of this subject for many years, and has done much to educate users of pipe-lines to the importance of oxygen elimination in their pipe systems. I am also in agreement with much that Mr. Aston's paper has set forth, and I am glad that the younger men are taking up these studies and carrying them forward. I think we must admit, however, that in spite of all our scientific generalizations on this subject, the publication of which has extended over a great many years, corrosion troubles are still going on and that we still find it difficult to predict failure in advance or to guard against it. A steam-pipe may burst down in the bowels of a battleship and men may die horribly, scalded to death, because a boiler-tube has

failed from corrosion in one particular spot. Corrosion is continually going on in every metal that is put into the strenuous service of modern civilization. Whether we will ever be able with all of our knowledge to entirely prevent financial loss and danger through corrosion, I very seriously doubt. That we can, however, do much to obviate these difficulties, I am more than ever convinced. Our added knowledge has led to stricter control under specification, and much of the imperfect metal that used to go easily into service is now subject to rejection. I believe that the corrosion problem is based primarily on the metallurgical study of production of sound metal from the original ingot. I believe this to be true whether we happen to be interested in the metallurgy of iron and steel or brass or any of the other commercial metals. If metals are to have a long life and comparative freedom from failure, we must have homogeneity in the original metal from which the service unit is manufactured. I am trying to forget tonight the more or less acrimonious discussions that some of us have engaged in in the past, as to whether it is the influence of this element or that element, or this impurity or that impurity, which is the fundamental cause of success or failure, and I will try to emphasize the responsibility that falls upon the shoulders of metallurgists who are charged with the care taken in the original manufacture of the metal, to the end that it shall be as homogeneous and as free from deleterious impurities as possible. What the world needs for carrying on its work is sound, homogeneous metal, free from gases and blow-holes, free from that condition which one may run into after the metal is rolled down or flattened out, which I have sometimes tried to define as "metallic gas sandwiches." If the original ingot of a metal contains blow-holes, the rolling of the metal into any form whatsoever does not eliminate this gas, which must find room for itself somewhere in the metal. Whether corrosive action is due to electrolysis or not, it seems to me to be perfectly evident that metal of this kind would not have the endurance under service conditions that a perfectly homogeneous, gasless metal would have.

We in America are not alone in the attention being given to these important studies. In Great Britain, through the British Iron and Steel Institute, the Faraday Society, and the Institute of Metals, there is a large contemporary literature on corrosion subjects, and most of these societies have special committees appointed to study them. Government commissions in England and in other nations have been appointed to study and report, for it is fully recognized that the insidious attacks of corrosion may in the long run affect the efficiency of battleships, submarines and other arms, and thus very possibly turn the tide of success or defeat at some strenuous moment. The conservation of our metals and their protection after they have been manufactured and put into service, is one of the most important scientific problems of the day.

Frank N. Speller: The point which impresses me most in Mr. Aston's experiments is the striking manner in which these data illustrate the predominating nature of surface conditions on pitting. This has, as he says, been brought out in other investigations which show clearly that dissimilar conditions on the surface of metals exposed to moisture and air produce electrochemical reactions which result in corrosion, irrespective of the composition of the metal.

It is important for engineers to appreciate this point and not to expect too much from the metallurgist. They can do much more themselves, for instance, in the designing of piping systems to conserve the life of the metal than can the metallurgist, and at less cost, but to do this they must understand the fundamental principles of corrosion and not be led into a false state of security by the quack advertising found these days in popular magazines.

The engineer and architect should know why corrosion inside of a tank or water-pipe system is relatively different, even with the same materials, than corrosion on a roof, and that conclusions cannot be drawn from experiences with one condition and applied to the other. If such facts are appreciated in their full significance most of the differences of opinion found among engineers will be explained, and we will make a long step in advance.

In regard to Mr. Aston's observations on the effect of rust itself, I believe he is correct in the main; *i. e.,* initial rusting renders the underlying metal anodic. However, we have usually found that rust which has been forming for several months is electro-negative to the iron, even though the rust was not allowed to dry. Nevertheless the peculiar pitting found in water-pipe indicates anodic action on the part of rust. The pits form where the mill scale has been removed, and over each a mound of spongy rust is found. The pitted area is evidently anodic to the surrounding surface.

A paper presented at a joint session of the New York Section of the American Electrochemical Society and the American Institute of Electrical Engineers, in New York City, March 10, 1916. Called up for discussion at the Twenty-ninth Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

THE INFLUENCE OF FREQUENCY OF REVERSAL OF CURRENT ON ELECTROLYTIC CORROSION.

By Burton McCollum and G. H. Ahlborn.

[Abstract of Paper.]*

Since most of the electrolysis which occurs in underground metallic structures is due to stray currents from electric railways, and since only a small percentage of these operate with alternating current, it might seem at first thought that alternating current electrolysis is of rather infrequent occurrence, and that the problems connected with it do not deserve much attention. However, in addition to the railways which use alternating or reverse currents as motive power, such currents often result as an incident of railway operation. These occur not only in the ordinary negative systems of railways as mentioned above, as the trolley load shifts from point to point on the track with the movement of the cars, but they occur to a greater extent and in a much larger territory in the case of negative return systems in which insulated negative feeders are used. In such systems the potential differences between pipes and tracks can be greatly reduced, but this is accompanied by a large increase in the area of the so-called neutral zone in which the polarity of the pipes is continually changing from positive to negative. With certain types of three-wire systems which are now being seriously considered in some places for the prevention of electrolysis, there will be large areas in which the polarity of the pipes will fluctuate between small positive and negative values. It has also been proposed that with the usual type of return that the trolley be made alternately positive and negative on succeeding days or weeks. All of these methods would have the effect of reversing the current flow on underground structures, and the period of the cycle would vary from a few seconds to a day or longer.

* The full paper has been published by the American Institute of Electrical Engineers.

The data discussed in this paper were obtained as a part of the general investigation of electrolysis conducted by the Bureau of Standards. Its object is not to determine the laws which govern electrolytic corrosion at any one frequency, but to take a standard set of conditions approaching as nearly as possible those existing in practice, that is, wrought iron pipes and lead sheaths imbedded in soil and to determine the corrosion which will occur in the range of frequencies mentioned above, namely, for frequencies ranging from 60 cycles per second to a week or more per cycle. These data will be of material assistance in determining the effectiveness of many of the proposed systems of electrolysis mitigation.

In this paper the term "coefficient of corrosion" is frequently used in connection with the corrosion of an anode. This factor is the ratio of the actual corrosion observed to that which would have occurred if all of the electrode reactions determined by Faraday's law had been involved solely in corroding the anode.

Soil: The soil used was natural soil near the Bureau of Standards—a light clay having a resistance of 8000 ohms per centimeter cube at approximate saturation. It will support a good vegetable growth and is a fairly normal soil.

Chemicals: Five sets of tests were run with 0.5 percent of sodium carbonate added. The rest with only the natural soil, kept moist.

Electrodes: The corrosion of different kinds of iron does not differ by large percentages under the conditions of these tests, and since "American iron," which is Bessemer process steel, is obtainable in convenient form it was adopted. This material was fine-grained and quite pure, having about one-tenth percent carbon and no slag. The lead was commercially pure, and on analysis was found to contain traces of tin or antimony. Indoor specimens were 5 by 5 cm. square, the iron being about 0.5 cm. thick and the lead 0.2 cm. thick. The outdoor iron specimens were 20 cm. square and about 0.2 cm. thick.

The mill scale and oxide left on the materials in the process of manufacture were not removed, since it was felt that with alternating current the surface might affect the corrosion considerably more than with direct current.

Frequency of Reversal: Eleven series of tests were run, with reversals every 1/60, 1/15, 1, and 6 seconds, 1, 5, and 10 minutes, 1 hour, 2 days, 2 weeks, and, for check, a direct current.

Current Density: One-half a milliampere per sq. centimeter.

CONCLUSIONS.

1. The corrosion of both iron and lead electrodes decreases with increasing frequency of reversal of the current.

2. The corrosion is practically negligible for both metals when the period of the cycle is not greater than about one minute.

3. With iron electrodes a limiting frequency is reached between 15 and 60 cycles per second, beyond which no appreciable corrosion occurs. No such limit was reached in the lead tests, although it may exist at a higher frequency than 60 cycles.

4. With periodically reversed currents, the addition of sodium carbonate to the soil reduces the loss in the case of iron and increases it in the case of lead.

5. The coefficient of corrosion of lead, under the soil conditions described in the report, when subjected to the action of direct current was found to be only about 25 percent of the theoretical value.

6. The corrosion of lead reaches practically the maximum value with a frequency of reversal lying between one day and one week.

7. The corrosion of iron does not reach a maximum value until the period of the cycle is considerably in excess of two weeks.

8. The most important conclusion to be drawn from these investigations is that in the so-called neutral zone of street railway networks where the pipes continually reverse in polarity, the damage is much less than would be expected from a consideration of the arithmetical average of the current discharged from the pipes into the earth. Where pipes are alternately positive and negative with periods not exceeding 10 or 15 minutes, the algebraic sum of the current discharged is more nearly a correct index to the total damage that will result than any other figure that can readily be obtained.

9. The reduction in corrosion due to periodically reversed currents appears to be due to the fact that the corrosive process is

in a large degree reversible; so that the metal corroded during the half cycle when current is being discharged is in large measure redeposited during the succeeding half cycle when the current flows toward the metal. The redeposited metal may not be of much value mechanically, but it serves as an anode surface during the next succeeding half cycle, and thus protects the uncorroded metal beneath.

10. The extent to which the corrosive process is reversible depends upon the freedom with which the electrolyte circulates, and particularly, on the freedom of access of such substances as oxygen or carbon dioxide, which may result in secondary reactions giving rise to insoluble precipitates of the corroded metal. It is largely for this reason that the corrosion becomes greater with a longer period of the cycle, since the longer the period the greater will be the effect of these secondary reactions.

Bureau of Standards,
Washington, D. C.

DISCUSSION.

(*At New York, March 10, 1916.*)

Philip Torchio: The most important results in the findings in these investigations are, first, that with ordinary frequencies, of 25 to 60 cycles, the corrosion of underground structures is practically nil. In this country some of the water companies are still objecting to having the electric lighting companies ground their neutrals to the pipes of the water companies. I think that the results of the investigation of the Bureau of Standards should dissipate any fear of trouble due to the grounding of neutrals to the water pipes.

The next important point brought out by the paper, which should dissipate another fear, is that with potentials in a certain zone changing from positive to negative, which fluctuation may occur in periods represented by the passing of a car, with time intervals of possibly five or ten minutes, the corrosion would be negligible.

The next important conclusion to be drawn from the paper is rather astonishing. I refer to it seriously proposing to ameliorate electrolysis conditions by reversing the polarity of the trolley at certain intervals, as, for instance, of one hour, or a day, or even a week, and showing that by so doing the damage by electrolysis may be reduced to one-tenth, or one-quarter, of what it would be by keeping the trolley potential constant, as we are accustomed to do. This suggestion is not a new one. It cannot be ascribed to ignorance that this method has not been tried, because as far back as 1902 a Danish engineer, Mr. Absalon Larsen, published in the Elektrotechnische Zeitschrift, of September, 1902, the results of his tests made in the Copenhagen Polytechnic Laboratory, and also a field test, both carried out on practically the same lines as those by Messrs. McCollum and Ahlborn presented to us tonight. Making allowance for the immeasurably greater details and completeness of the investigation of Messrs. McCollum and Ahlborn, and also the more complete scientific methods of procedure, it is astonishing that the results obtained in Copenhagen fifteen years ago are in their broad general lines confirmed by the results of the work in the Bureau of Standards.

In Mr. Larsen's paper he states, briefly, that with one reversal per day the electrolytic action can be reduced to one-quarter, and by one reversal per hour it can be reduced to one-thirtieth of its normal value. From the tables given in tonight's paper we see that the results with one reversal every two days would be on the order of one-quarter, and one reversal every hour be on the order of one-tenth; it is, therefore, broadly speaking, astonishing that in fifteen years no use whatsoever has been made of the suggestion presented by Larsen.

Two years ago the Joint National Committee on Electrolysis reported on European practice. I made a survey throughout certain of the European countries, and before starting from America I consulted with Dr. Rosa on what line of investigation I should follow, and on his suggestion I had prepared a list of questions to ask every one I interviewed. As a result of all of the interviews I had in England, France, Germany and Italy, I found that this suggestion of the reversal of potential was practically never adopted. The only places where the potential of the trolley has

been reversed were in St. Gall and Nürnberg, but that was done only once, to try to remedy electrolytic conditions. In all other cases practically no application has been made of this suggestion, which appears to promise great benefit in many bad electrolysis situations.

Alfred F. Ganz: Several papers have been published describing the results of experiments with alternating currents of commercial frequencies in producing electrolysis of iron in soils and in solutions. The results of these experiments have generally shown that with alternating current some corrosion results, but that this is only of the order of one percent of that calculated by Faraday's law from the quantity of electricity discharged from the anode. The present authors have found substantially the same results with alternating currents of frequencies of 15 and 60 cycles per second. These authors have also included tests using direct current which was reversed at relatively long intervals, the period varying from one second to two weeks. They have found that even with the longest period of reversal, the corrosion produced is less than that computed by Faraday's law from the total quantity of electricity leaving the anode, and that the corrosion of both iron and lead electrodes decreases with increasing frequency.

The authors have used a current density of approximately 0.5 milliampere per square centimeter for the iron and also for the lead samples, which is approximately 0.46 ampere per square foot. This current density is probably from 10 to over 100 times as great as generally found in practice in the case of pipes and cable sheaths affected by stray currents. The authors state that this current density was used because in a previous investigation on the corrosion of iron in street soils it had been found that with current densities no greater than this coefficients of corrosion of practically unity were obtained with direct current. I would like to ask the authors whether similar tests were made in the case of lead, and if so, whether with much smaller current densities a coefficient of corrosion as low as 25 percent was also found. It is well known that as the density of current flowing from a corrodible anode to an electrolyte is increased, a point is reached where, in addition to the metal going into solution,

gases are formed, so that only part of the electricity is effective in dissolving the anode and the other part produces gas. If tests with lower current densities on lead samples have not been made, it seems to me that this should be done before the conclusion can be accepted that with lead as an anode the corrosion is only 25 percent of that calculated by Faraday's law.

The present tests were made with only one kind of soil. It is entirely possible that with soils containing other constituents than the soil used a higher coefficient of corrosion may be found for lead.

Assuming, however, that the corrosion from electrolytes with lead anodes is under practical conditions only 25 percent of that calculated by Faraday's law, it seems to me that this makes alternating or infrequently reversed currents much less advantageous in the case of lead than is indicated by the coefficients of corrosion given for these currents, in the paper. To make clear what I mean, I find in Table No. 8 that with a frequency of reversal of 10 minutes, the average coefficient of corrosion is given as 0.132. This figure is obtained by dividing the actual loss from electrolysis by the loss calculated by Faraday's law. If, however, with direct current the coefficient of corrosion is 25 percent instead of 100 percent, the beneficial effect of a frequency of reversal of 10 minutes is represented by four times 0.132 or by 0.528, and not by 0.132. This means practically that if with direct current a certain amount of corrosion is produced, a reversing current at frequency of 10 minutes will cause a little more than half as much corrosion. As it is well known that lead cable sheaths in practice are very rapidly destroyed by localized pitting, where they are at all times positive to earth and even where a relatively small current flows from the cable sheaths, it is evident that much less improvement is to be expected from alternating or from infrequently reversed currents in the case of lead cable sheaths than is indicated by the coefficients of corrosion given in the paper.

The authors state that the reduction in electrolytic corrosion from alternating or infrequently reversed currents appears to be due to the fact that the corrosive action is in a large degree reversible. While the results of the tests indicate that this may be the action, I do not believe that they are sufficiently conclusive

to prove this theory, and it would be very desirable to have this phase of the subject discussed theoretically from an electrochemical standpoint. This is to my mind extremely important, because it may serve to answer the question as to whether the low coefficients of corrosion found in the present tests may also be expected with the widely varying conditions of the electrolyte found in practice. I may say that I have seen examples of rapid corrosion of iron from electrolysis where the iron was continually reversing in polarity to the earth. It may, however, be that in these cases the total quantity of electricity discharged from the iron was much greater than the total quantity of electricity flowing to the iron.

On the basis of the very low coefficients of corrosion found where the reversal is one minute or less, the authors draw the conclusion that where underground pipes or cable sheaths reverse more or less continually in polarity the algebraic average of the current or potential is more nearly a correct index of the total damage that would result from electrolysis than any other figure that can be obtained. All of the tests described in the paper were, however, made with reversed currents whose algebraic average is zero. In order to prove the validity of the algebraic average for judging danger from electrolysis, it seems to me that it would be desirable to make experiments in which the algebraic average is other than zero, and particularly with reversed currents in which the periods for the positive loads are made substantially longer than the periods for the negative loads.

From a practical standpoint it seems to me that it would also be very misleading to give only the algebraic average of the potential or current, where these quantities continually reverse. This will readily be seen from the fact that large currents may reverse in underground cable sheaths or pipes, and yet the algebraic averages may be zero, so that if the results are expressed only as algebraic averages, an entirely false impression is created. There are other dangers from stray currents flowing in underground pipes and cable sheaths besides electrolysis, as for example fire hazard from sparks or arcing where currents pass through buildings on service pipes or cables. These dangers are not in any sense measured by the algebraic average of the currents.

I want to say in conclusion, that if the low coefficients of corro-

sion found by the present authors, even with very slowly reversed currents, are substantiated for soils generally and for the low current densities usually met in practice, methods of electrolysis mitigation which result in large areas of reversing polarities of the underground structures, such as insulated return feeder systems and three-wire systems, assure a much greater degree of protection from destruction by electrolysis of these structures, and particularly of iron structures, than has previously been expected. The work described by the present authors has therefore wide practical application, and it is fortunate that we now have the results of this work available.

J. L. R. HAYDEN (*Communicated*): I agree with the author's conclusions except in some minor features. I do not believe that there is a limiting frequency beyond which no appreciable corrosion occurs. While at 25 cycles the corrosion is already less than 1 percent in most cases, there is still a distinct decrease at 60 cycles, the traces of electrolytic action seem to remain even at very much higher frequencies. At the low-current densities used in the experiments the chemical corrosion is comparable with the electrolytic, and the chemical corrosion is very variable; a serious source of error therefore results at these frequencies, which in my opinion is the cause of the apparently negative corrosion at 60 cycles, in Table V.

I agree with the experience that alkaline solutions chemically protect iron, but attack lead.

The low coefficient of corrosion of lead may be apparent only, and due to the assumption of lead as bivalent. As in the lead storage battery the anodic action proceeds at PbO_2, it appears probable that with uni-directional current of long duration lead shows a valency of 4. This would double all the corrosion coefficients of lead. At higher frequencies lead probably is bivalent, and this would account for the different slopes of the lead and the iron curves.

The observer's results seem to agree with my experience that iron is more erratic than lead. This I explained by the ease with which iron can assume the passive (probably trivalent) state. As time, current density (even momentary), previous history and nature of electrolyte (nitrates favorable, chlorides unfavorable for passivity) and surface condition (presence of scale) have

a material influence on passivity ("Electrolytic Corrosion of Iron by Direct Current," Journal of Franklin Institute, October 1911), during half cycles of long duration the iron electrodes may change from active to passive and inversely. As active iron appears to be bivalent and passive iron trivalent, the previous hydrogen electrode, when changing to anode by reversal of current, would tend to start active. This may account for some of the differences between the odd and even electrodes.

As nitrates and ammonia are frequent constituents of soil, and nitrates have a strong passive effect, it would have been interesting to make some experiments with soil containing ammonium nitrate, for instance.

Also, the action of higher current densities would be of interest, especially with lead electrodes. Lead cables laid in ducts are usually fairly well insulated except locally, where moisture penetrates, etc. With such lead cables the current flow may be localized, and then higher densities result.

S. M. Kintner (*Communicated*): The practical value of the information sought, in so far as it relates to engineering practice, in most instances at least, is in determining what will happen to a pipe or lead-covered cable buried in the ground and subjected to such electrolytic actions. A pipe or cable under such conditions fails by a small hole, or at least only a small hole is sufficient to cause serious trouble very shortly. This being the case, it is of rather academic than practical interest to know whether the pipe as a whole has lost one percent in weight, or even ten percent.

Even if we knew quite accurately how the loss varied with current density, etc., we could make no practical use of it, in an application such as that assumed, for the very evident reason that we have no control over the current distribution as it goes to or from such a buried pipe. What we are interested in, however, is the order of the loss that may be expected compared to that due to direct-current electrolysis, or to ordinary corrosion under like conditions of soil.

The paper contains some very interesting results on the effects of infrequent reversals of direct current. These results are of considerable practical value, if applied with proper discretion.

In a series of tests of alternating-current electrolysis made by

me in 1904-5, and reported in part in the Electric Journal of 1905, attempts were made to use iron and lead plates, weighed accurately before and after testing them. The plates, of iron in some test boxes, and lead in others, were arranged so as to form the two ends of small boxes, of which the other sides were made of wood. Some 20 or 30 of these were used in various combinations of frequencies, of electrolytes, of current densities, etc. It did not take long, however, to show that the current densities varied greatly, that the "gain" plates of the direct-current cells lost as much as, or more than, those plates subjected to the simple corrosion or to the alternating electrolytic action, and that the cleaning for weighing was apt to produce greater losses than the losses it was expected to detect.

First the direct current "loss" plates would be eaten through at places slightly below the surface, while at other places down deeper in the solution the action was comparatively slight. This was quite conclusive proof that the current densities were not uniform over the whole plate surface. The mounting employed was expected to eliminate the greater density at the edges of the plates and thus secure a closer approximation to uniformity of current density.

It is to be noted that in the present paper no such precautions were taken, and so it is reasonable to expect even a greater variation in current density than in the tests made by me in 1904.

After concluding a number of the plate tests, all laboratory tests, and reaching the decision that no data of a greater degree of refinement was obtainable, or even if it could be obtained could not be applied practically, it was decided to check the general observations by tests approximating as nearly as possible to actual operating conditions. A number of pipes about four feet long and three inches in diameter were buried, after being carefully weighed, marked and having their ends sealed with an asphalt gum. These pipes, both commercial wrought iron pipe and lead cable, were buried in three different localities, separated some twenty-five miles from each other. These test pipes were arranged in groups in each of the three localities and in this way the effects of frequency, current density (in so far as total current per pipe would indicate it), direct current and simple corrosion were observed. Pipes were buried at different depths varying from

two to six feet. There was a sufficient number of pipes in each combination to permit the removal of some after various lengths of action. They were all removed at the end of one year.

Attempts at weighing and checking against the original weights proved of no value whatever. A careful study did show that effects of the alternating-current electrolysis, with both 25 and 60 cycle, were just about the same as that shown by pipes subjected to corrosion only. Fortunately the character of soil, in the three places in which they were buried, differed very materially. The effects on the pipes followed quite closely, in each of the three places, that produced by corrosion only. The serious effects noted were pits, some quite deep, while the pipe immediately adjacent was in good condition with no signs of pit marks. The pits were no different on the pipes subjected to the alternating current than those where corrosion only had caused the action. This indicates either a variation in the pipe or a variation in the soil in which it is buried, which sets up a strong local activity.

Carl Hering (*Communicated*): The results given in the paper are of interest and of value, especially as some of them are different from what was supposed to be the case, while others confirm by experiment what heretofore was a mere belief. One of the most valuable results is that in what are called the neutral districts in underground electrolytic corrosion problems the periodic reversals of current practically neutralize each other; also that corrosion from underground alternating currents of the usual frequencies, is not a serious menace; there were good reasons for believing that for lead-covered cables, at least, the corrosion due to underground alternating currents might be serious.

Asa P. Way (*Communicated*): This paper suggests an attempt I made about six years ago for the mitigation of electrolysis. In this method an especially designed transformer was used, through the low voltage side of which passed the return current of one or more pipe-drainage feeders connected to taps for different potential. The primary was excited by an intermittent current from a 550 volt D. C. source, through resistance. The idea was to set up a relatively low-frequency reversing potential between pipes and rails.

I have had in mind for some time to use the principles set forth

in this paper in connection with the insulated negative feeder system, but particularly with such an installation put in operation about two months ago. In this particular installation two of the feeders connect to a track about 4,000 feet apart, where the tracks are consistently negative to water pipes, although conditions are not dangerous, due principally to some poor track-bonding in the neighborhood. My idea is to place in series with each of these feeders a definite amount of resistance alternately to be short circuited by automatically operated contactors. The resistance would be so designed that when one is short circuited and the other is in series with the other feeder, or *vice versa,* the potential between pipes and rails at the ends of the feeders would alternately reverse. It might be found that proper resistance in series with the return current of both feeders could be alternately short circuited and left in series, which would probably increase the area subject to reverse current flow between pipes and rails. The contactors could be operated by a relay controlled by a sign flasher or any other convenient method. I would like to know if the authors of this paper think that this would be effective.

C. B. Martin: The tests described in this paper were made in soil. This condition is the usual one that must be considered in connection with standard trolley roads, but in connection with electrified heavy traction roads the effect of reversing currents upon steel embedded in concrete becomes of importance.

For the last twenty-five months we have had under test units made of one-inch steel rods, six inches long, surrounded by two inches of concrete placed in water baths in metal pails. In some of these units the current has flowed in the direction to produce electrolysis of the rod, and in others the same current was reversed at the rate of 0.8 cycles per minute. The resistance of the D. C. units increased steadily; that of the reversing units hardly at all.

How well the steel embedded in concrete of the D. C. unit automatically protected itself was shown by the reduction of the current with the same impressed potential. At the start the current flow was 0.08 ampere, in ten days 0.04, in thirty-four days 0.02, in three hundred and twenty-eight days 0.01, and in seven hundred and sixty days 0.005. The efficiency of corrosion for the whole period was 28.4 percent.

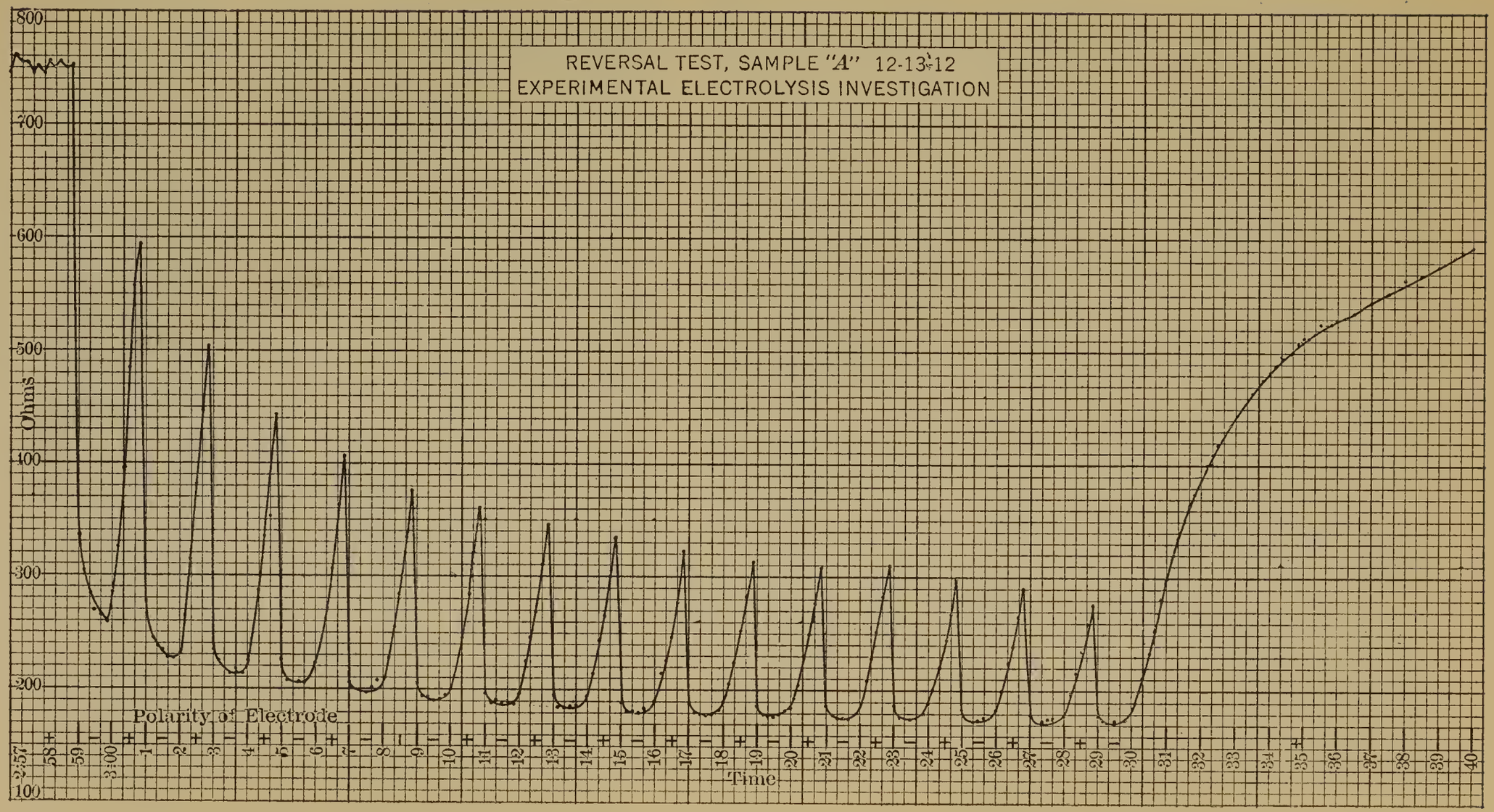
The average current flowing was 0.053 milliamperes per sq. cm. of the surface of the rod, which is about one-tenth of that required to produce the maximum corrosion of iron. This low density is, however, very much above that encountered upon the steel structures in which we are most interested.

An examination of the reversed current electrode showed that it was but slightly affected. Only 0.588 g. of metal had been removed, and the efficiency of corrosion was only 0.95 percent of the positive current flowing.

The results of our reversing tests on steel in concrete therefore agree very closely with the results reported in the paper on reversing tests in soil. In both cases the resulting electrolysis is practically negligible.

Another test which we made in 1912 is interesting. An electrolysis test sample similar to those described above which had been under test for three weeks, with a positive potential on the electrode increasing from 12 volts to 52 volts as the internal resistance of the sample increased, was subjected to a current reversing every minute, and the varying resistance of the circuit recorded. (See Fig. A). Very promptly upon the reversal of the current there was a surprising drop in the resistance, which was partially restored upon again making the electrode positive. Under repeated reversals the resistance of the sample steadily decreased with every indication that a stable condition had been reached. Finally the electrode was again subject to a steady positive potential, and the resistance increased to approximately its original value. Naturally, the question arises what caused the resistance to increase in this manner? Was the action due to gases or the expulsion and return of the electrolyte? At any rate the test shows that the resistance of the electrolytic circuit of steel encased in concrete is built up by making the steel positive, and broken down by making it negative.

Electrolysis engineers working to protect underground structures from electrolysis have constantly before them the statement that one D. C. ampere flowing steadily for a year will disintegrate twenty pounds of iron, or seventy-five pounds of lead under favorable conditions. Should such rates of deterioration be realized in practise many important structures would be in need of


REVERSAL TEST, SAMPLE "A" 12-13-12
EXPERIMENTAL ELECTROLYSIS INVESTIGATION
Ohms
800
700
600
500
400
300
200
100
Polarity of Electrode
Time
2:57
58
59
3:00
1
2
3
4
5
6
7
8
9
10
11
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14
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Fig. A.

extended repairs, and the expenditure of very large sums in protective measures would be justified.

When, however, foundations, especially steel foundations encased in concrete, have been uncovered and found to be but slightly affected although subjected to a potential favoring electrolysis for years, the question naturally arises whether there are not circumstances which in practise largely reduce these large estimates of electrolysis damage.

A conclusion that should be drawn from the paper is that in an electrolysis survey readings should be taken for twenty-four hours, preferably by means of recording instruments, so that the full cycle of a day's operations will be included and all current reversals recorded.

We are particularly interested in the statement that the loss of lead in soil under D. C. flow is about 25 percent of the theoretical loss. We trust that this important phenomenon will be more fully investigated and explained. Tests which we have made upon electrolysis samples of steel surrounded by two inches of concrete indicate that the efficiency of corrosion is not over 30 percent. Some of these tests have extended over long periods.

Referring to conclusion 2 of the paper, that "the corrosion is practically negligible for both metals when the period of the cycle is not greater than about one minute," we have understood that when electrolysis is taking place under ordinary conditions, water molecules are broken up and the gases collect at the anode and cathode surfaces. Upon reversal of current, is it not possible that these gases, especially the hydrogen gases, in some way interfere with the prompt starting of electrolysis? May it not take about a minute to dissipate these gases?

In the twenty-five-months' test referred to above, there was a period without flow of current between each reversal amounting to about one-third of the time.

Thomas M. Roberts: Referring to conclusion 8, Fig. B represents a rise of potential in a pipe-line above a given zero, and a simultaneous drop of potential in the rails with the going and coming of cars. It is to be noted that the change of potential of the conductors in the earth is greater as the distance between the

bond points increases. This probably is known to many railway engineers, but it is not so well known to many who install underground systems of piping which may become bonded with electrical conductors. I simply call attention to the fact that in an active zone a well-bonded system of pipes and conductors suffers less from electrolysis than a poorly-bonded system. This we know irrespective of whether the electrolytic effects are caused by an arithmetical average or by the algebraic sum of the currents. The effect is what it is irrespective of the name given to the cause. The name is a small matter; the method of installation is the important thing.

Another point, though not a direct corollary, is worthy of mention here. It covers the expenditure of the financial bonds which enable the electrical bonds to be made. Here the engineer should

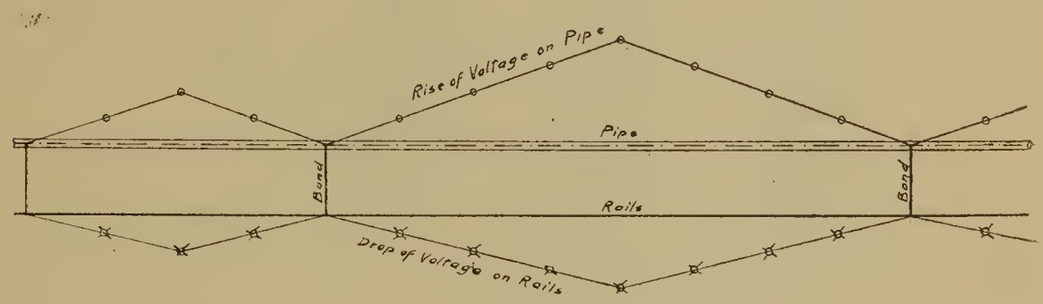

FIG. B.

have a part. The pipes should be well bonded together in series, as well as the rails, and the two separate conductors again well cross-bonded. This means in a broad sense, that they should be well financially loaded as well as metallically bonded; for when the financiers have raised the wherewithal for any gas-pipe or water-pipe extension, what set or group of men can direct the proper use of the money better than the electrical engineers? The better the engineer the better the bond will be made, and the better the bond the less the sum of the currents which cause electrolytic action.

THOMAS SPOONER (*Communicated*): Almost a year ago we made some tests on the effect of frequency of alternating current on the rate of corrosion of various metals and alloys in solution of 2 percent sodium carbonate and in sea water. The tests were largely qualitative, but they may add something of interest to this subject.

The investigation was made on plates of various materials immersed in electrolytes contained in beakers. There was no stirring beyond that produced by the electrolytic action. Each plate had an immersed area (one side) of about 2.7 sq. in. (17.4 sq. cm.) and the average current varied from 5 amperes to 1 ampere, the higher values being used only on a few preliminary tests. The average currents for most of the tests was about 2, with various frequencies from 25 to 0.1 cycles per second. The results are expressed in loss in weights in grams per ampere-hour. Some of the results obtained are as follows:

TABLE A. *Electrolyte—2% Sodium Carbonate.*

LOSS IN GRAMS PER AMPERE HOUR.

Frequency Cycles per sec.	*Ingot Iron	Monel Metal	Nickel-Chromium Alloy	Current Supply
0.1	0.0175	0.0008	0.0021	Reversing Switch
0.1	0.0155	0.0014	0.0030	Revolving Rheostat
0.2	0.0055	0.00077	0.0030	"
0.5	0.0021	0.00084	0.0017	"
1.0	0.0011	0.00056	0.00078	A. C. Generator
5.0	0.00015	0.00011	0.0022	"
25.0	0.000012			Shop Supply

* Ingot iron was tested in sodium carbonate solution with D. C. It was badly corroded at end of 9½ hours.

TABLE B. *Electrolyte—Sea Water.*

0.1	Badly corroded in 3½ hrs.	Badly corroded in 3½ hrs.	Entirely eaten away in 3½ hrs.	Revolving Rheostat
1.0	0.0041	0.0111	.0498	A. C. Generator
5.0	0.0022	0.0098	.0401	"

A few tests were made on a 5 percent nickel-steel alloy (rolled), a 5 percent nickel-steel alloy (case), and boiler plate. The first two corroded rapidly, while the last at frequencies of 0.5, 1.0 and 5.0 and in a 2 percent sodium carbonate solution gave the same results as ingot iron, within the limits of accuracy of the test.

The first 0.1 cycle tests were made with a motor-driven reversing switch, which was open about the same length of time it was closed. The revolving rheostat tests were made with an apparatus as shown in Fig. C. The operation of the device is obvious from the figure. It gave a wave like that shown in Fig. D.

The resistance R^2 (Fig. C) was introduced to correct a slight dissymmetry in the positive and negative halves of the current wave. This device was substituted for the reversing switch, be-

cause it was difficult to make the time of closure of the switch the same for both directions, and because for this particular investigation it was desired to have the wave form approximately a sine. The average value of the current was determined by an integrating D. C. ammeter which was reversed each half cycle. The ratio between the maximum current and this average was calculated and considered constant for the several succeeding tests. The equality of the positive and negative halves of the current wave was checked by means of a copper coulometer.

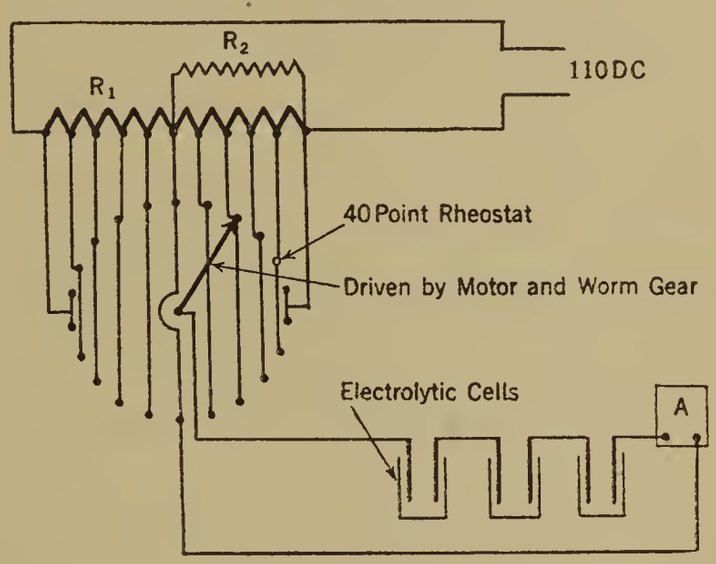

Fig. C.

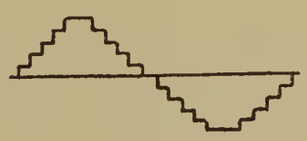

Fig. D.

These tests led us to the following conclusions:

(a) The lower the frequency the greater the loss in weight of the electrodes, this loss increasing very rapidly below 0.5 cycle per second.

(b) All of the substances investigated corroded very rapidly with D. C. currents.

(c) Where considerable chlorides are present in the electrolyte, ingot iron seems to be superior to any of the other substances investigated.

(d) With low frequencies, monel metal seems to be the most satisfactory with 2 percent sodium carbonate solution.

(e) Boiler iron seems to have almost the same loss as ingot iron.

(f) Very large differences in loss were obtained, depending on the condition of the surface of the plates. This may account for the peculiar increase in loss for the nichrome at 5 cycles (see Table A) as this material is especially susceptible to surface conditions.

Some previous investigators have thought that the electrode loss per hour was a function of the current density. Where they have shown data to substantiate this, is it not possible that the greater current density produced a stirring action, which, as pointed out by the authors of this paper, increases the loss.

Alexander Maxwell: I think the authors of this paper should be congratulated for their investigation of this very practical phase of the general subject of corrosion of underground structures by stray currents, particularly with regard to that part of the investigation which deals with reversing continuous currents, as distinguished from alternating currents of the ordinary frequencies. It is too often assumed that serious corrosion occurs only where the affected structures are close to the rails and positive in potential to them, whereas corrosion is frequently found in the so-called "neutral zones," as well as in locations remote from railway structures, in the latter case corrosion being due to exchange of current between different piping or cable systems, very often associated with reversals of direction.

In one respect, however, I desire to offer a criticism, repeating a similar comment of mine in connection with an earlier paper of one of the authors, namely, that the current densities employed are much higher than those encountered in practice. To be sure, the authors have offered a good reason for the current density employed, but it seems especially unfortunate that lower densities were not investigated, on account of the uncertainty which remains regarding the precise nature of the corrosion where low corrosion coefficients were found.

Two examples taken at random illustrate the magnitude of the apparent current densities which may be met in practice, associated with actual corrosion. In one case current having a 24-hour average value of 3.4 amperes, flowed from a 20-inch cast-iron gas main between two test stations, 150 feet apart. This

works out to 0.0046 milliampere per sq. cm. as an average over the whole surface. Therefore, only about 1/100 of the whole surface would be conducting to attain the current density used in the experiments described in the paper.

In another case, serious damage was done to cable sheaths by the loss of one ampere in a single section between manholes. Since the cable was of large diameter, it may be assumed that the lowest 1-inch of circumference was in contact with moisture and soil in the conduit, the minimum distance between manholes was about 250 feet. Under these conditions the contact area would be 19,350 sq. cm., and the average current density would be 0.052 milliampere per sq. cm., or roughly, 1/10 of the value used in the paper.

I do not mean to say that densities as low as these average densities should necessarily be employed for experimentation, but that something approximating them should be employed in view of the admitted influence of secondary effects which greatly increase the corrosion coefficients at low densities, and which might strongly influence an investigation like the present one. Moreover, it should be borne in mind that the average current densities referred to above may still be directly compared with the densities used by the authors, since theirs are also average densities.

Burton McCollum (*Communicated*): Mr. Torchio has raised the question as to why the principles brought out in the paper have not been heretofore applied by electric railway interests for the mitigation of electrolysis troubles. The reason I think is quite apparent, namely that in order to secure anything like the high degree of protection that would be desired it would be necessary to reverse the polarity of the trolley several times a day, although, of course, reversing once every 24 hours would accomplish something. To reverse the polarity of the trolley once an hour or oftener would introduce an operating complication that few, if any, railway men would consider. Such frequent reversal would be objectionable even where an entire system is supplied by a single station, and would be practically prohibitive in the case of a railway system fed by several interconnected stations. It is largely for this reason, I think, that the work of Mr. Larsen has not been given more attention. I would point out in this

connection that the work described in the present paper covers an entirely different field and was undertaken for an entirely different purpose from the work done by Mr. Larsen. Mr. Larsen's object was to determine whether or not it would be feasible to reduce electrolysis trouble by a frequent reversal of the trolley polarity, and he carried out no experiments in which the current was reversed more frequently than once an hour. In the present investigation it was our aim to determine the order of magnitude of the corrosion that would be produced in the so-called neutral areas of railways where the reversal takes place at short intervals of from a few seconds to a few minutes. In order to make the investigation complete we carried out some experiments with alternating currents of ordinary frequency on which a good deal of work had previously been done, and also extended our investigation into the region of long periods such as those adopted by Mr. Larsen. Between these extremes, however, we have covered a wide range which has not heretofore been investigated, namely, frequency of reversal such as those found between tracks and pipes and other underground structures in the so-called neutral areas of electric railways.

I wish to make it clear that the authors have not put forward this data with any idea that it will be used as the basis of a comprehensive system of electrolysis mitigation, and we do not consider that there is much likelihood of it being used in this way for the reasons pointed out above. Our principal purpose in bringing out the results of these is to show that in so-called neutral areas the actual amount of corrosion that will take place is much less than has often been supposed, and that the extension of the neutral areas due to the application of insulated return feeders, three-wire systems, and other methods of mitigating electrolysis troubles, need not be regarded as introducing any additional hazard to underground structures.

Regarding the criticism brought out by Prof. Ganz and Mr. Maxwell, I would say that the current density of 0.5 milliampere per square centimeter was used for the reason that this is about the lowest value that is likely to be of any practical consequence. If the current density is 0.5 milliampere per square centimeter the actual rate at which the iron would be corroded away would be approximately one centimeter in 12 years. This is a rate of

corrosion which is frequently encountered in practice where electrolysis conditions are only moderately severe. Much higher current densities are frequently found, however; on the other hand, it is perfectly true, as Mr. Maxwell and Prof. Ganz have pointed out, that in practice, especially near the so-called neutral zones, the current density may often be out a very small fraction of that used in the tests, it must be admitted that such current densities are of no practical importance. For instance, if we use a current density of 0.0046 milliampere per square centimeter, which Mr. Maxwell states has been actually found by him, it would appear that it would take about 1300 years to corrode the iron to a depth of one centimeter. While it may be true that the effect of reversed currents with these low-current densities may be very different from those observed in these experiments, it is evident that the rate of corrosion in any case will be so low that it is of no concern from a practical standpoint, however interesting it might be from a purely scientific point of view. In this connection I would say that the corrosion on the test specimens used by the authors, while not strictly uniform, was nevertheless so well distributed over the surface that it was evident that the current density at any one point was not very greatly in excess of the average value of 0.5 milliampere per square centimeter used in these tests.

Prof. Ganz states that the tests were made in only one kind of soil. This is quite true. Part of the tests were made in the natural soil and some with sodium carbonate added, and the results, while slightly different, indicate the same general law. It is not improbable that with soil from different sources it would be found that the knee of the corrosion curve, or the point at which it begins to rise abruptly, would be shifted more or less. Nevertheless all of the experiments available indicate that the effects would be of the same general character as here observed.

Prof. Ganz quotes some figures from the table and seemed to convey the impression that they are misleading. For example, he states that the table shows that with a ten-minute reversal in the case of lead the coefficient of corrosion given is 0.132, and he appears to assume that this is intended to show that the ratio of the corrosion on this frequency to the corrosion on direct current would be 0.132. This error might readily creep in provided the

authors did not give the actual corrosion on direct current, but since this is given and shown to be approximately 0.25, I do not see how any one could be misled as to the magnitude of the reduction in corrosion produced by the reversals.

Prof. Ganz also suggested that in view of the fact that all of the experiments described in the paper were made with periodically reversed currents in which the algebraic average was zero, that it would be desirable to make additional experiments with unsymmetrical alternating currents in which the algebraic average is not zero. This I think is a good suggestion and I hope that it may be possible to make such experiments in the near future.

Mr. Way described a plan which he expects to try out whereby he hopes to utilize the principles set forth in the paper for reducing electrolysis troubles. If I understand his plan correctly, it would amount to superposing on a uni-directional current a symmetrical alternating current of sufficient magnitude to reverse periodically the polarity of the pipe. This would not have the effect of reducing the algebraic average of the current, so that if I have not misunderstood his plan I do not see how it would materially reduce electrolysis troubles.

Mr. Chubb suggests that possibly the positive and negative half waves were not equal and that this may in part account for the large discrepancy in some cases between the corrosion of the odd and even electrodes. This seems very unlikely since great care was taken to avoid any error of this sort. An oscillographic record carefully analyzed in a considerable number of cases did not reveal any appreciable unbalance.

I have been particularly interested in the results presented by Mr. Spooner, as they were made under different conditions using a liquid electrolyte instead of soil, but nevertheless the results obtained on ingot iron are substantially in accord with the results presented in our paper.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

SOME FAULTS OF THE SMALL ELECTRIC-ARC FURNACE FOR MELTING AND REFINING STEEL.

By W. M. McKnight.*

The small electric arc furnace is rapidly coming into favor for the production of small, highly-refined steel castings, and its advent is welcomed by both the manufacturers of steel castings and the electric power companies. Without going into the merits of the electric furnace as a competitor of the crucible furnace and open-hearth furnace, regarding the quality of the product or regarding it as a welcome load builder for power companies, I wish to point out some of the handicaps to its universal adoption and successful operation.

Process.

The furnaces that are now in operation in several parts of this country, while differing in some respects in their mechanical construction and electrical demands, all refine the steel by the same chemical process; *viz.,* by raising the temperature of the bath to 2,500° C. or better, by boiling the metal to eliminate the impurities, and by the introduction of the necessary refining agents to bring it up to the fineness desired.

Construction.

All small arc furnaces are constructed on certain general mechanical lines, as follows: The furnace consists of a steel shell mounted on trunnions for tilting to discharge the molten metal. This jacket is lined with a highly refractory lining, sufficiently thick to retain the heat; the lining and shell, however, are pierced with port-holes for the purpose of charging the furnace with steel, adding the refining agents, discharging the refined metal and for inserting the electrodes, and all these port-holes furnish avenues of escape for the heated gases. The electrodes are

* Southern California Edison Company, Redondo Beach, California.

secured in place by the holders mounted on the tilting shell, and the holder raises or lowers the electrode by hand operation, by hydraulic control, or by electric motor control.

Efficiency.

In spite of the fact that the electric furnace, today, is turning out small castings of a better quality and at a lower cost than by other processes, nevertheless, the over-all efficiency of the best furnaces on the market is far from 100 percent.

There are three principal sources of loss:

Electrical: In the improper delivery of the energy to the metal.

Mechanical: In the improper design of the furnace shell and ports, to exclude cold air and retain the heat.

Chemical: The improper combinations of refractory materials, that should be inexpensive in first cost, withstand the intense heat long enough to avoid delays through the interruption of the manufacturing process, and not introduce any chemical combination with the metal. Also, there should be found an electrode that will not waste away too rapidly through oxidation, within and without the furnace, as it comes in contact with the air and gases.

Electrical conditions can be improved by supplying the proper current at the proper potential. Mechanical conditions can be improved by re-designing detail portions of the furnace. The chemical conditions can be improved only by exhaustive research and careful study.

Refractories.

Refractories are of two kinds: the heat-resisting linings and the heat-producing electrodes. The heat-resisting linings may be either acid or basic, depending on the degree of heat required for the quality of steel to be turned out. The heat-producing refractories may be either carbon or graphite.

Temperatures.

Merely to melt down steel scrap and turn out castings of semi-steel and low-grade castings of unknown quality does not require a temperature of 2,500° C., and for a furnace for this class of work an acid lining of silica is successfully used. To refine

the steel, however, it is necessary to use a basic lining of magnesite, at least where it comes in contact with the bath, or where the heat would be intense enough to melt down the silica and cause it to run down into the bath and combine with the metal bath or slag and the basic lining, thereby changing their character.

Lining.

The furnace linings can be put in in two ways: build up with brick work, the bricks made to conform to the shape of the shell and laid up in a basic paste or coal tar binder, or the material for the lining may be made up into a mass and rammed into the shell. The brick lining offers some advantages, inasmuch as it has passed through a glazing process that should prolong its heat-resisting qualities, but it is expensive, particularly if special sizes and shapes are desired, and if the source of supply is remote, and the delivery uncertain.

The rammed lining should be superior from the fact that it is, if properly put in, a monolithic mass, hence there should be little danger of the bath breaking through to the shell, with the resulting damage to the furnace and loss of the batch.

Electrodes.

Electrodes are of two kinds: carbon and graphite. Each has its merits. The carbon electrode is the less costly, but has less electrical carrying capacity than graphite, and consequently must be greater in cross-section to deliver the same amount of energy. It therefore has a larger amount of radiating surface, and consequently the saving in first cost of the carbon is offset by the loss in energy dissipated in heat. Owing to the intense heat of the electrode, its surface both within and without the furnace shell loses carbon by its surface contact with the air and resulting oxidation.

The graphite electrode, by virtue of its greater carrying capacity, is smaller in diameter, and offers less surface for radiation of heat and oxidation. The electrode within the furnace shell is subject to further attack by the passage of the electric current through the heated gases to the lining, which, at a temperature of 2,500° C., itself becomes a very good conductor of electricity.

CONCLUSIONS.

Electric steel castings may not be better in quality than those turned out by skilled operators with fuel furnaces, but small electric steel castings can be made at a less cost under present conditions, which conditions could be improved, and then the furnaces will be limited only by the capacity of the source of the supply of electrical energy.

The field has apparently no limitations, if the chemist can overcome the losses I have pointed out. Formulate a better refractory lining, an electrode that will not waste away except in heating the bath, and utilize the waste gases by manufacturing them into a by-product or by-products.

I have only touched on one single product which gives promise of so much for the electric furnace. The field is undeveloped and has almost unlimited possibilities. In three Pacific Coast States alone, I am informed, there is approximately 1,000,000 horse-power in water-power going to waste, because a too zealous government is retarding its development, by capital ready and willing to invest, if more liberal terms of lease can be secured. Such terms might be forthcoming if the American Electrochemical Society would bend its energies to make efficient power consuming devices.

This certainly is the day for the chemist, and his greatest achievements will be in the electrochemical field.

DISCUSSION.

J. W. Richards: On page 301 the temperature of the bath is spoken of as 2,500° C. That is about 1,000° too high. The electric furnace is supposed by some people to make steel at much higher temperature than is used in the open-hearth or the Bessemer, but that is not necessarily so, and the majority of the electric steel furnaces are run at about the same temperature as the open hearth. While you can, theoretically, heat the charge up to 1,900° or 2,000° C., in doing so you would probably melt the roof of the furnace, so that the practical limitations of temperature in the electrical furnace and the practical temperature desirable to attain are very little, if any, higher, than in the ordinary open-hearth and Bessemer processes.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

THE RENNERFELT ELECTRIC ARC FURNACE.

By C. H. Vom Baur.

The Stassano furnace was the forerunner of the Rennerfelt. The former started with a radiating arc, playing almost horizontally over the bath, whereas the latter furnace forces the naturally large arc flame violently down on the charge and away from the roof by employing a different method of electrode arrangement. Polyphase current of any frequency and voltage is used.

The advantage of a solid bottom has long been recognized, and the extensive use (33 in operation and 20 building) which this furnace has been put to in less than four years, is largely due to this feature in conjunction with the first-mentioned characteristic.

The Rennerfelt furnace idea is shown diagrammatically by Fig. 1.

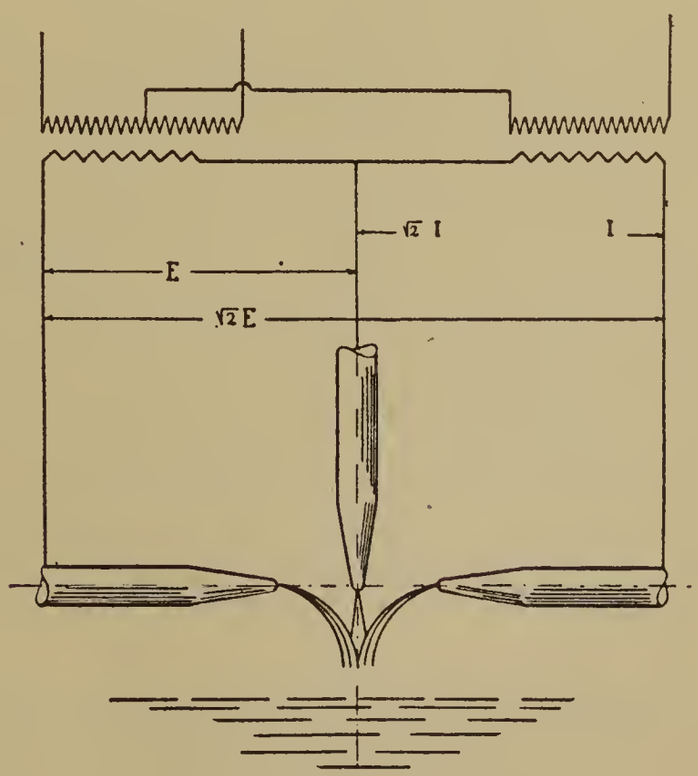

Fig. 1. Electrodes and Connections.

The almost universally used 3-phase current is shown entering the transformers and is changed by means of Scott connection to 2-phase 3-wire system. The middle or combined conductor carries about 40 percent more current in the vertical than in either of the side electrodes, and this forces the entire large radiating arc, by the resolution of forces and electro-magnetic action, down on the bath. This form of arc has hitherto been unknown in electric furnaces. The horizontal electrodes are about 15 inches (38 cm.) above the bath or slag, in some of the larger size furnaces, and the operating distance from tip to tip of the horizontal electrodes is usually from 18 to 22 inches (45 to 55 cm.) or more. These dimensions give an idea of the size of the flame, which, striking the bath, mushrooms to the sides and ends of the furnace. The heat reaching the roof is consequently very indirect, thus favoring low roof-maintenance costs. These low roof-refractory costs have often proven themselves in practice; for instance, when melting cold steel scrap and making tool steel quality, heats taking 5 to 6 hours in a low-power furnace, at about 150 kw. per ton capacity of the furnace, the roof has lasted 192 heats with a 9 inch (23 cm.) brick. With faster melting and the 12 inch (30 cm.) brick, more heats could be expected per roof.

The furnace is built in different sizes. The first 30 furnaces were three tons and under capacity. Since then, a four-ton has been placed in operation and a second is expected to follow shortly. Eight-ton furnaces are building, while 12-ton and larger furnaces are being contemplated. Rennerfelt believes that with the mutiple arc system, as years ago proposed in principle by Stassano, electric furnaces of 40, 50, and even 75 tons capacity can be made, and run to give satisfaction. This type of multiple arc furnace is shown by Figs. 2 and 3. A 40-ton furnace for instance would have four sets of electrodes of three each, the side electrodes 6 inches (15 cm.) and the top 7 inches (18 cm.) diameter, the furnace taking 4,800 kw. at the terminals. The inside diameter would be about 7½ feet (230 cm.) and the hearth proper about 14 feet (420 cm.) long.

On account of the peculiar characteristic of the Rennerfelt arc, it is very steady with hand regulation, and the furnace operation is electrically simplified to a marked degree, by avoiding all auto-

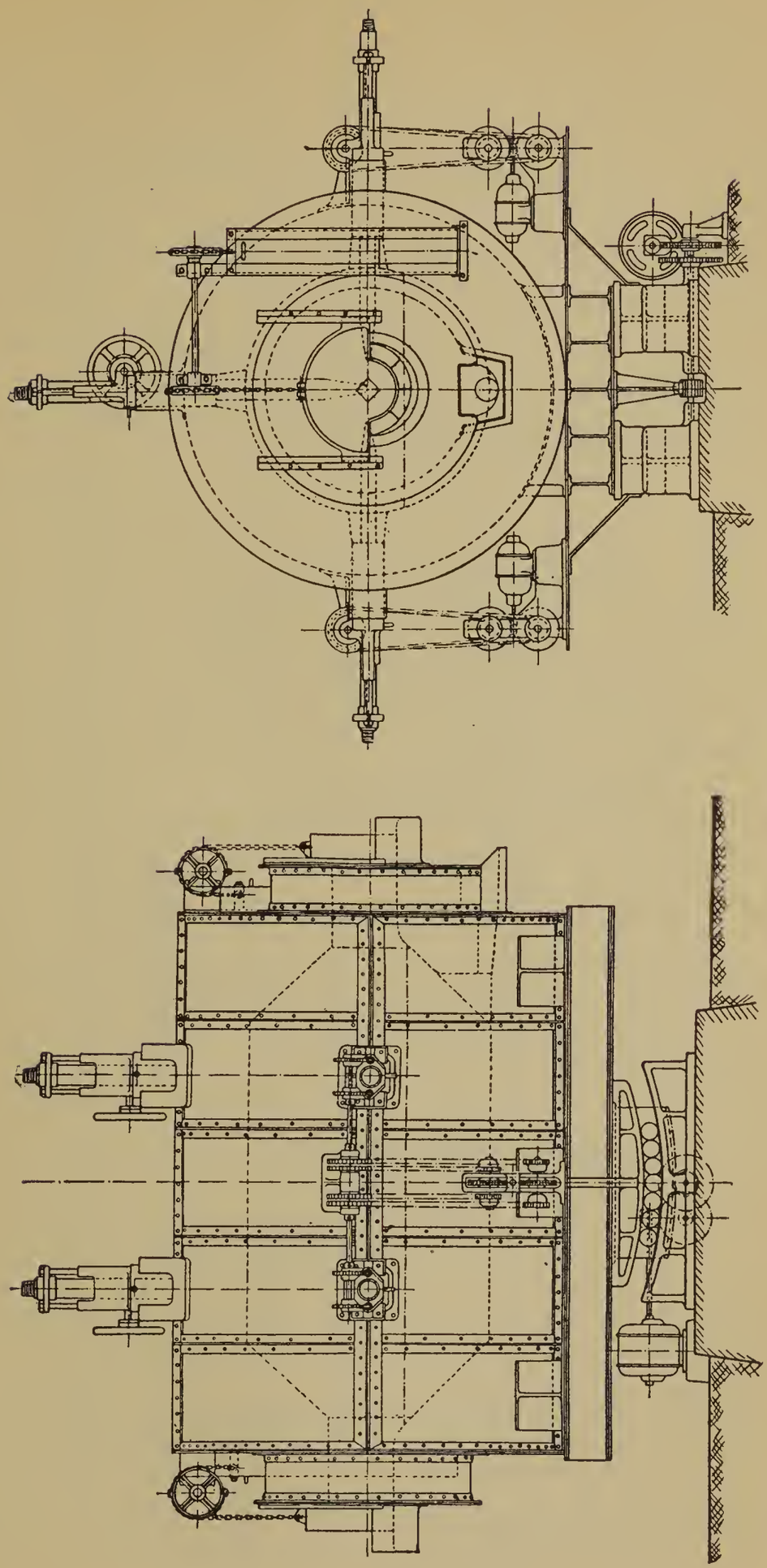

FIG. 2. Twelve-ton Furnace.

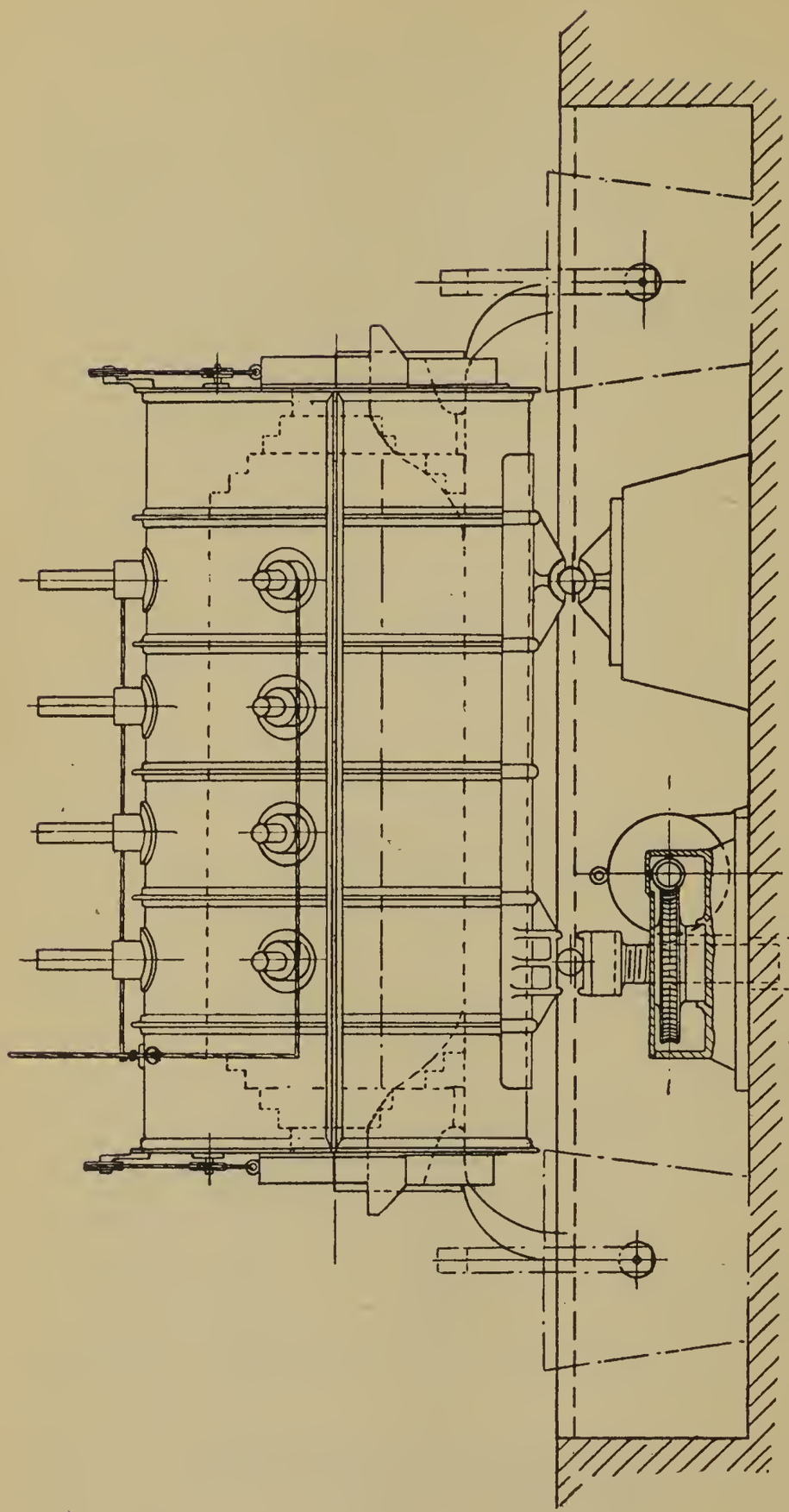

Fig. 3. Forty-ton Furnace.

matic electrode regulation, although motors with push-button control are contemplated. As only 4 or 6 pounds (1.8 to 2.7 kg.) of Acheson graphite are burned away per ton of cold steel scrap or pig melted and treated, it is evident that the electrode regulation with such a steady arc, made between three points of stability, that is, the tips of three electrodes, is a minimum, and this has been proved in practice. The electrodes oftentimes do not have to be adjusted for a half hour, and still the power consumption is about as steady during these periods as with an induction furnace. Light metal scrap or turnings can be heaped in the furnace with the electrodes touching the charge, and yet before many minutes the free-burning arc between the electrode tips has established itself.

All but three or four of these furnaces are operating, or contemplate doing so, with basic bottoms. Only a few operate with acid bottom, and these in tool steel works where the highest class of raw material is available at reasonable prices. The bottoms of these furnaces last as long as similar solid bottoms of open-hearth furnaces. The sides burn away a little faster and wear away also, due to the slag action, and the roof goes faster than the sides, but lasts as long as previously mentioned.

The wear of the electrodes seems to depend on three things: first, the density of the current; second, the circular area and length exposed inside the furnace; and third, the amount of air leaking into the furnace. The latter cause seems to have the most deleterious effect and hence doors are fewer now than formerly. Up to the three-ton size there is only one door and that over the spout, all other furnaces have but two doors and these are much tighter. The clearance of the cooling boxes is also made less. Only ⅛-inch (3 mm.) clearance is allowed, which is just enough room to compensate for the slight irregularity in the manufacture of what are ordinarily perfectly round electrodes.

The electrical conditions are most satisfactory, as evidenced by the opinions of Central Station managers. On account of the high power factor at 50 to 60 cycles, it being 90 to 97 percent, the phase displacement is almost entirely avoided, and the phases are almost perfectly balanced.

The so-called efficiency of electric furnaces depends, as has been

broadly discussed by Hering and others, on the rate at which the heat is forced into the furnace, besides upon good insulation, proper painting, etc. The main point of these is the rate at which the power is consumed. Three or four years ago, 200 kw. was considered ample for a one-ton furnace; now 350 to 375 for this size is common practice. Consequently the melting time has decreased and the kw. hours per ton are less, the cost of the steel in the ladle is less, and the output is correspondingly increased. The practical limit to this high-powering of furnaces is the power of the refractories to withstand the higher heat for sustained periods, the refractories are also subjected to greater differences of temperature between heats, especially with those furnaces where the electric current cannot be maintained while there is no charge in the furnace.

With low-powered Rennerfelt furnaces the power consumption when treating various metals has been as follows:

Melting red brass	168	kw.h. per metric ton
" pure copper	197	" " " "
" white iron	290	" " " "
" gray iron	325	" " " "
" 80% ferro-manganese	441	" " " "
" steel scrap, not ready to pour	455	" " " "
" and "killing" steel scrap on an acid bottom, about	600	" " " "
" and refining steel scrap on a basic bottom, about	700	" " " "
" 80% ferro-manganese and holding, tapping and charging	741	" " " "
Making 67% ferro-tungsten, small scale	5,730	" " " "

The characteristic features of the furnace may be summed up as follows:

(*1*) The heat is generated with an arc with the absence of exceedingly hard strains on the power supply.

(*2*) On account of the steady power and on account of the large flame widely diffused, as shown in Fig. 4, the heat is communicated to the charge quicker than with arcs of the thin-pencilled type, made between the tips of the electrode and the bath.

(*3*) A large flame or a series of them sweeps all over the major portion of the charge in the center of the furnace, or at regular distances along the major axis of the furnace, and is directed and violently deflected downwards.

(*4*) The heat being thrown downward in this way and being a radiating arc of large volume, these are features favoring higher efficiency, other things being equal, and the roof therefore has a long and satisfactory life.

(*5*) There is only one small hole in the short-radius roof for each set of electrodes, both of these features making for strength and lower maintenance cost.

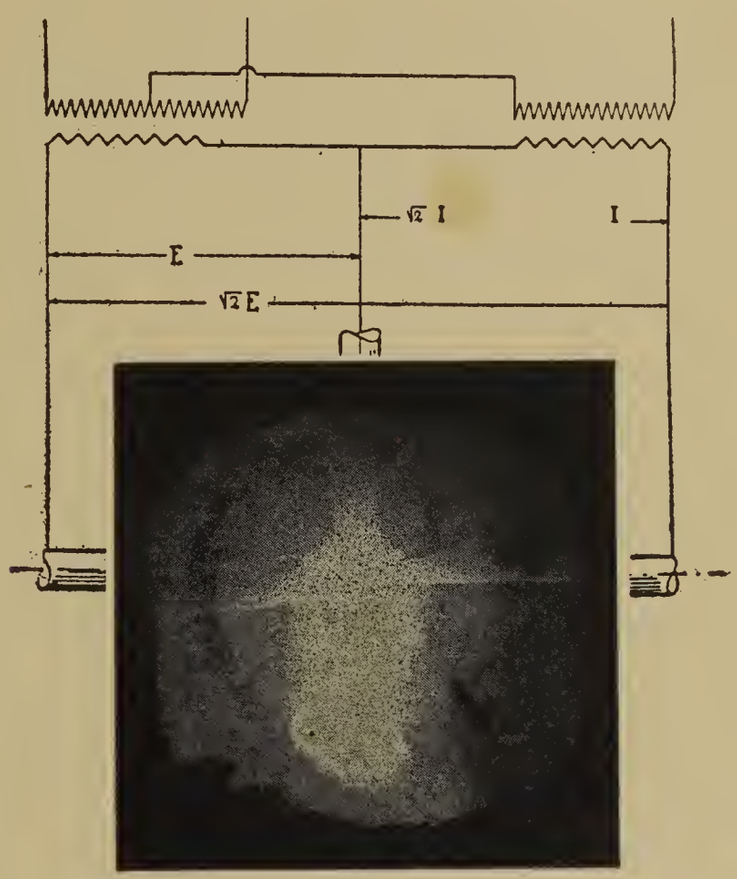

Fig. 4. The Rennerfelt Arc

(*6*) The hearth is more easily surveyed and accessible, during operation, than in arc furnaces having electrodes only 2 or 3 inches (5 to 8 cm.) above the slag.

(*7*) With larger furnaces multiple arcs are used, this method starting in with the 6-ton furnace. The heat distribution is markedly better than with arc furnaces of equal size, using the metal to conduct the current in one form or another.

(*8*) The heat is applied more directly, although the arc is not.

(*9*) The heat gradient in an electric arc is greater if it takes place in the widely-spread-out heating zone rather than in a narrow space.

(*10*) The radiating arc is a much more rapid way of transmitting heat than the slow heat of conduction of other arcs.

(*11*) There is no water-cooling below the bath, which consequently avoids danger of explosions from this source.

(*12*) The voltage at the arc is from 75 to 100, depending on the furnace size, and these potentials are harmless if a shock is experienced.

(*13*) The amperes per electrode in large furnaces is small, namely, only 5,400 and 7,700 in a 3,600 kw. furnace, whereas with other three-phase and three-electrode furnaces this would approach, at 80 percent power factor at 110 volts, 23,600 amperes. This higher amount of current brings with it difficulties of the skin effect, because these larger currents have to be brought to single electrodes.

(*14*) The hearth bottom is burned in by the arc without the use of coke or other material.

(*15*) The electric current can be kept on the furnace during tapping and charging, thus keeping the furnace at a more uniform temperature, with its consequent advantages of keeping the refractories from checking. The furnace thus does not cool down and a saving of 10 to 20 minutes in time can be made on this account per heat, this being the usual charging time; whereas most other electric arc furnaces have the current shut off during the charging period because it is unavoidable.

DISCUSSION.

N. Petinot: Mr. Vom Baur states that in the Stassano furnace the arc plays nearly horizontally above the bath. In my experience with such a furnace, I found that after the melting period the arc plays directly on the slag, as if the metallic bath was a magnet attracting the arc. Of course, during the boiling after an addition of iron ore, the arc is temporarily submerged in the slag. Consequently, the Stassano furnace would seem to have the same advantage as is attributed to the Rennerfelt fur-

nace, without requiring a vertical electrode to direct the arc to the bath. In the Stassano furnace the electrodes are not horizontal, but have a slope of 45 degrees.

I wish also to ask how the lining of a basic Rennerfelt furnace is constructed. Usually in basic furnaces the hearth is made of magnesite or dolomite material, and the roof is made of silica brick. I take it for granted that all the electric arc Rennerfelt furnaces are cylindrical in form, as shown in the illustration of the 12-ton and 40-ton furnaces. Where, in such furnaces, does the roof start, or, where is the line separating the basic from the acid walls? When the roof is gone is it necessary to tear down the whole roof, and if so, how far?

Mr. Vom Baur states that more heats may be expected from a roof 12 inches (30 cm.) thick than from a roof 9 inches (23 cm.) thick. Theoretically, one would think so, but practically it is generally found that in furnaces of the arc type, such as Heroult, Girod, etc., during the first days of operation there is a rapid destruction of the roof, until its thickness is reduced to about 4 inches (10 cm.). It seems that at this point the outward cooling of the top prevents further rapid destruction.

The electrode consumption is given as 4 to 6 pounds (2 to 3 kg.) per ton of steel made. I wish to ask if such figures are an average of a long run, taking into consideration the temporary shutdowns, heat absorbed by the furnace, and chances of broken electrodes, which unfortunately happen once in a while. In case the feeding of the electrodes is not continuous, do such figures allow for the butts?

Mr. Vom Baur states that the furnace uses graphite electrodes. I wish to ask what advantage they have over amorphous electrodes. Major Stassano always told me that he got better results from amorphous electrodes, and it is a fact that he does not use graphite electrodes in any of his furnaces.

In the characteristic features of the Rennerfelt furnace, paragraph 6, it is mentioned that the hearth is more easily surveyed and accessible during operation than in arc furnaces having electrodes only 2 or 3 inches (5 to 8 cm.) above the slag. As Mr. Vom Baur states that Rennerfelt furnaces up to 3 ton capacity have only one door over the spout, I cannot see how this con-

struction makes it any easier to survey the hearth, or more accessible for patching the lining, than a Heroult furnace having three doors placed on different sides.

Mr. Vom Baur mentions in paragraph 10 that "the radiating arc is a much more rapid way of transmitting heat than the slow heat of conduction of other arcs." This statement needs clarifying. It is difficult to see why heat developed by the arc in a Heroult or Girod furnace should be considered transmitted by conduction any more than in the case of the arc in a Rennerfelt furnace.

In paragraph 14, Mr. Vom Baur mentions as an advantage of the furnace that the hearth may be burnt in by the arc without the use of coke or other material. I do not see any disadvantage in using coke or gas for this purpose, since they are far cheaper than electric power, especially as in making a new basic bottom a very high temperature is not required, only enough to fuse the binder used to hold the crushed magnesite together, such binder being usually basic slag or iron ore.

I wish to ask one more question. With the experience gained from the thirty-three Rennerfelt furnaces in operation, and particularly from those with a basic bottom, does the Rennerfelt furnace perform only a melting operation, or does such a furnace perform a melting operation first and then a refining one? I do not mean by refining only the lowering of the sulphur and phosphorus contents, but also thorough deoxidation of the steel, and is this performed in the furnace itself without further help of deoxidizers, as aluminum, added, in the ladle? Such a deoxidizing feature has been widely advertised by electric-steel furnace manufacturers as one of the main advantages gained over the same grades of steel manufactured in basic open-hearth furnaces of the same capacity, where the same low sulphur and phosphorus content can be obtained, but where the deoxidation has to be completed in the ladle.

C. H. Vom Baur: While I was in Bonn, Germany, some years ago, on a two-day visit, I saw the two Stassano furnaces in operation, and my remarks were based on what I saw there. There was a peephole through the door, and it appeared to me that the flame was only slightly bowed horizontally over the bath,

and several inches away from it, but the flame was not touching the bath, as it does in the Heroult and Girod types. The roof brick of these Stassano furnaces was made of magnesite of special shape, and the roof lasted one week. At that time magnesite bricks were cheap, but even then the expense per ton of steel melted was $2.00 to $2.30 for the refractories.

In the Rennerfelt furnace, even with the roof of magnesite brick, the cost of refractories has not been over seventy or eighty cents a ton, including everything.

The roof comes off in one piece, and is now lined with silica, but previous to the war we could get and used magnesite brick. The latter were used almost exclusively; even though they spalled they lasted longer, and the cost per ton was less than with silica.

It is true that a silica brick roof will burn away at first very rapidly. Twelve-inch (30-cm.) brick have been tried, and the roofs seemed to last longer, but it is not customary to use this size. Nowadays it is less a question of the cost per ton than of the annoyance caused by replacements of the roof, and so these roofs are being made of several sizes of brick to ascertain the most satisfactory size.

When making tool steel from cold material in a low-powered furnace where the heats take six or seven hours, we use not more than 6 lb. (3 kg.) of electrodes per ton of steel made. In making steel for castings, where the heats take about four hours, we got down to 4 lb. (2 kg.) of electrodes per ton, when using Acheson graphite.

F. A. J. FitzGerald: Did that include the butts?

C. H. Vom Baur: Jointed electrodes were used, and therefore there were no butts.

When burning in a new hearth it is advisable to first make a wood fire to heat it up, afterwards the arc can be used to sinter. By doing that we saved having a coke fire in there for two or three days.

As to seeing inside the furnace, the door is very wide, so that one can see practically all parts of the furnace except the sloping part going up towards the spout, and even that can be seen if the furnace is tilted a little. We think it is an advantage to have

only one door in a furnace of three tons or smaller, because Wills and Schuyler, who made a test on one of the Heroult furnaces at Easton, Pa., found a door radiating 20 to 40 kilowatts (Trans. Amer. Electrochem. Soc. (1915) **28**, 207).

N. PETINOT: Does the furnace perform a melting and deoxidizing operation? If so, how?

C. H. VOM BAUR: The furnace melts, deoxidizes and refines the same as other electric furnaces, and the procedure is much the same as in a basic open-hearth furnace. Was there any special operation that you had in mind?

N. PETINOT: How do you deoxidize in your electric furnace? The open-hearth furnace practice is a continual oxidizing operation.

C. H. VOM BAUR: First, during the dephosphorizing period the steel is purposely made what is called "rotten steel," with iron oxide or roll scale or something similar, then the slag is removed and a lime slag put on. Then ferrosilicon and ferromanganese additions are made. Thereafter it is a question of getting the slag in the right condition, not too acid and not too basic.

N. PETINOT: During the deoxidizing period do you change your slag as is done in the old arc furnace?

C. H. VOM BAUR: Yes.

N. PETINOT: Is the slag composed absolutely of burnt lime?

C. H. VOM BAUR: Lime and sand.

N. PETINOT: Why do you use sand?

C. H. VOM BAUR: Sometimes the lime slag gets too thick, and we want to thin it out. Sometimes we use some fluorspar.

N. PETINOT: Why use sand in your slag; it must cut your basic lining?

C. H. VOM BAUR: It is sometimes cheaper to put in sand than fluorspar.

N. PETINOT: Do you deoxidize by ferrosilicon?

C. H. VOM BAUR: Yes.

N. PETINOT: What else?

C. H. VOM BAUR: Not having any oxidizing flame going down on the bath, to bring oxygen into the steel, we found we did not have to use so much ferrosilicon in order to deoxidize thoroughly.

N. PETINOT: But after you have removed the oxidizing slag your bath is saturated with oxide. Now, if we start from this point, how do you take care of the oxide? By an addition of ferrosilicon?

C. H. VOM BAUR: Surely, you have to put in ferrosilicon.

N. PETINOT: Only ferrosilicon?

C. H. VOM BAUR: We put in some ferromanganese, too.

N. PETINOT: Nothing else?

C. H. VOM BAUR: Sometimes we make a very low manganese steel, in which you cannot use so much ferromanganese, and we have to use aluminum.

N. PETINOT: So you use ferrosilicon and aluminum to deoxidize your electric steel?

C. H. VOM BAUR: It depends on what steel you are making, it is very seldom that we use aluminum.

N. PETINOT: What is the advantage of the electric steel furnace over the ordinary open-hearth steel furnace?

C. H. VOM BAUR: The advantage is you can use the cheapest raw material and turn out from it tool steel. You cannot do that even in the crucible furnace.

N. PETINOT: No, you cannot do it with the crucible process, which is only a melting proposition, but you can do it in the basic open-hearth furnace.

C. H. VOM BAUR: In the open-hearth you cannot get phosphorus and sulphur down to 0.03, or something like that.

N. PETINOT: You will not, if you use a 50-ton or 100-ton open-hearth furnace, but if as operated in many places in Germany, you use a tilting furnace, you can tilt it back and take off your first slag, then add a second slag, made up of burnt lime and a little fluorspar as a thinner, and bring your phosphorus down to 0.010.

C. H. VOM BAUR: One hundredth?

N. PETINOT: Yes, and that is as low as ordinary crucible steel grades.

C. H. VOM BAUR: That is exceptional practice, whereas with the electric furnace you can do it as a regular thing. Another advantage of the electric furnace over the open-hearth furnace is that the steel is quieter.

N. PETINOT: That of course is proportional to the quantity of ferrosilicon and aluminum you use.

C. H. VOM BAUR: Not necessarily, you must always remember that we have a reducing atmosphere in the electric furnace, especially in one of the arc type.

CHAIRMAN FITZGERALD: I think the best way to settle this question is for you to explain in a written discussion just wherein the furnace has advantages for making steel over the open hearth; that is really the question.

J. W. RICHARDS: I think the difference between these two gentlemen is simply this—in the open-hearth furnace you have continuously an oxidizing influence upon the steel and the steel will not stay deoxidized. The very means of heating it keeps the steel continually oxidized in the open-hearth furnace, whereas in the electric furnace when you once deoxidize it it will stay deoxidized, unless you have some currents of air passing through the furnace, which should not happen.

Concerning the Stassano furnace, the arc is supposed to go from one carbon to the other without touching the bath. The only Stassano furnace I have seen in operation was at Turin. When Major Stassano was showing it to me, the arcs were jumping from each electrode to the bath, and back again to the next electrode, so that sometimes the arc does not work exactly in the way mentioned by Mr. Vom Baur in this first paragraph.

I am very much interested in the prospect of a 40-ton electric steel furnace, because I believe that the steel industry really needs a 40-ton or 50-ton furnace which will take the whole product of an open-hearth furnace, ready for casting, let us say, and will keep it hot and give it a dead melt. Such a furnace does not need to do refining, it does not need additions of ore, it should simply keep the steel melted during a half hour to an hour and

give it the effect of the dead-melting in the crucible. The electric furnace is particularly adaptable for that purpose, but we need a furnace large enough to take a full open-hearth charge and treat it at once. The Rennerfelt furnace seems adapted to that use, and if a 40-ton or 50-ton Rennerfelt furnace could be devised to do that, it would quickly find a place for dead-melting of open-hearth steel charges.

H. W. Gillett: The brass industry is becoming more interested in the electric furnace, particularly at the present time, on account of the crucible situation. Inasmuch as this paper will sooner or later percolate into the brass industry, I think it would be a good thing for Mr. Vom Baur to expand a little on the figures for red brass and copper. The figures which he gives are rather startling to some of us. After I got his figures on brass and copper, I looked up Rodenhauser and Schoenawa's book, translated by Vom Baur, p. 191, and found they take the theoretical heat requirements for melting steel scrap, at 489 K. W. H. per metric ton. The efficiency of the Rennerfelt furnace on steel figures up to 81.5 percent on that basis. If we assume that red brass or copper with lower temperatures would allow us in this furnace to get an efficiency of, say, 85 percent, and take the figures of Messrs. Richards, Hansen, Hering, and Clamer for the calculated power needed to melt red brass or copper, and correcting these figures to the average pouring temperatures for those materials (as the 10 percent above the melting point taken by Richards is too low for pouring anything but heavy, large castings), it figures out to an average of 165 K. W. H. per metric ton for red brass at 1150° C. In the same way, copper figures out about 205 K. W. H., at a pouring temperature of 1200°. A furnace at 85 percent efficiency would take about 200 K. W. H. per ton on red brass and 220 on copper. This means that the figures given for red brass and copper show about 100 percent efficiency in the Rennerfelt, which cannot readily be accepted without explanation. The figures for the theoretical requirements are inaccurate, of course, but I do not believe they are off much. The brass founder does not stop to think when he sees a figure given of 168 kilowatt-hours per ton, that this, if an accurate figure, must have been taken under abnormal conditions and can

hardly represent the average power requirement day in and day out. He is prone to think that these figures are what he can do in his own work and will represent his power bill.

It seems to me that figures given in this way ought to be explained so that people who are really looking for such a furnace will not be misled.

A. R. Calder: You will appreciate that this discussion is a most timely one when you consider that the price of ferromanganese is ten times what it was before the war started, the price of crucibles has gone up about four times, and they have deteriorated in quality about 50 percent.

Mr. Vom Baur has impressed upon us that this furnace has a reducing action, at least not an oxidizing action, which is unusually important in the melting of ferromanganese, and the resulting oxides are very injurious to the crucibles or the linings of the furnace.

Are the figures given in the paper as to power consumption correct? It states, white iron can be melted at 290 K. W. H. per ton, while ferromanganese takes 441 K. W. H. per ton. Metallurgically, this looks as though ferromanganese is rated too high, 50 percent higher than white iron. When melting, holding, tapping and charging ferromanganese, that is increased 50 percent, to 741 K. W. H. per ton of 80 percent ferromanganese.

Prof. Richards has touched on the refining of steel from an open-hearth furnace in some such furnace as described here this afternoon, and suggested that this could be accomplished by the transferring of the heat from the open-hearth into an electric furnace, and allowing it to stand and settle. That, I think, is a very good idea, but it seems to me that the recarburizers, alloys and deoxidizing materials should be added in the electric furnace after settling has taken place to get the greatest amount of efficiency out of the action.

De Courcy B. Browne: These furnaces are either basic or acid, and I would like to know what Mr. Vom Baur uses to thin the bath in the basic furnace and what in the acid. As I understand it, he anticipates using aluminum in the furnace, which would be difficult to do on account of the slag.

C. H. Vom Baur: As to Mr. Gillett's remarks about the figures

in Rodenhauser's book about 489 K. W. H. per ton for melting steel, that was based on what were then thought correct figures. Prof. Richards has since brought out figures much lower, and it seems to me in the case of the newer furnaces that Prof. Richards' figures prove more nearly true, namely, 347 or 348 K. W. H. per metric ton for melted steel. That is not true for pure iron. These furnaces, when they are high-powered, use 200 or 300 K. W. per ton capacity, and will run between 75 and 78 percent efficiency, sometimes as high as 80, depending on the temperature of the metal. I think that these older figures have been disproved. We have been making tests on all sorts of materials, and although the results may be changed further on, these figures are all based on practical experience in our furnaces. We believe that the instruments were accurately calibrated, within ½ percent.

C. H. Vom Baur (*Communicated*): The advantage which the electric furnace has over the open-hearth furnace and all other steel-making furnaces consists in the fact that you can make all sorts and all qualities of steel in the electric, even the highest qualities of crucible steel, without having to chose a pure or selected raw material. We can proceed, for instance, with the steel process in the electric furnace just as in open-hearth with the oxidation process, whereby we remove from the bath carbon, phosphorus, silicon, manganese, and some sulphur, whereupon the first refining slag is removed and it is then replaced with a non-refining slag, that is to say, by a slag which is low in oxides of iron, chromium, manganese, etc.

With certain well-defined combinations of this non-refining slag we may completely desulphurize and deoxidize the steel, that is, "kill" it, as in the crucible, by additions of silicon, aluminum, calcium, or by producing these elements in the furnace itself by taking them from the slag and by the proper reduction additions; but in contradistinction to the crucible melting, the bath can be held as long as desired at a high temperature, when the bath and slag have their correct chemical composition, without having any undesirable changes take place in the composition of the bath. Even when the finished bath contains easily oxidizable metals such as tungsten, chromium, silicon, vanadium, etc., the whole may be further heated under the blanket of slag, without in the least fearing a loss of these metals.

In addition to this, the oxidation process in the electric furnace can be carried out with greater surety than in any other melting furnace, because in this case we add the oxygen only in the form of ores, etc., in exact and determined quantities, and we can therefore keep the exact composition of the slag; whereas in the open-hearth furnace we never have complete control of the oxidizing influence of the gas. In the electric furnace we can already with the first refining avoid the over-saturation of the steel with oxygen. Another very great advantage of the electric furnace over the open-hearth is the possibility of having a very exact temperature regulation of the bath. Every steel man knows how valuable this advantage is.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, held in Washington, D. C., April 27-29, 1916.

THE BRITTLENESS OF ANNEALED COPPER

By W. E. Ruder.

In the process of manufacture of commercial copper, it has been found advisable to leave a certain amount of oxygen in the copper in order that it may retain the very desirable properties of ductility and mechanical strength. The ease with which copper takes up oxygen during smelting makes it necessary that this oxide be removed by the process of "poling," during which the oxide is reduced by the gases given off by the green poles. This process is carried on until only the small amount of oxygen necessary to produce "tough pitch" copper remains. This oxygen exists in practically all commercial copper, not specially deoxidized, in the form of Cu_2O and forms a matrix of eutectic around the primary copper grains.

It is common practice in annealing copper to maintain a strictly neutral or slightly oxidizing atmosphere. In the practice of the process of calorizing (Trans. Am. Electrochem. Soc., **27**, 253, 1915) it was found that copper articles became quite brittle even at temperatures as low as 500° C. In forging and working copper it is also necessary to have the atmosphere of the heating furnace pretty well regulated, or the whole lot will become unworkable.

Copper rail-bonds made up of strands of commercial copper wire, heated in an oil muffle during the process of manufacture, frequently and irregularly showed brittleness as though burned, but there was no sign of oxidation. It was assumed that the harmful effect was due to reducing gases from the fire which sometimes come into direct contact with the copper. To demontrate this, an experiment was tried as follows: Two quartz tubes were placed into a vertical electrically-heated furnace. One was closed and the other open at the lower end, while the upper ends of both tubes were open and extended outside the furnace. Commercial copper wires were placed in each of these tubes. Hydrogen gas was fed into the furnace and came into contact

with the wires in the open tube, but not with the others. The result of heating to red heat for ten minutes in this case was the apparent rotting of the wire in the tube open at both ends but not in the tube closed to the hydrogen.

Further evidence that this brittleness is due to the action of the reducing gases upon the dissolved oxygen is had from the fact that copper to which boron carbide or some other deoxidizing agent has been added does not show this effect. It is the purpose of this paper to report the result of a few experiments made to determine the effect upon regular and deoxidized copper, at different temperatures, of a few of the more common gases met with in practice.

Cuprous oxide may be reduced by hydrogen or carbon monoxide at temperatures as low as 200° C. Some effect must therefore be expected, even at temperatures below those usually employed in annealing.

In these experiments wires of plain 0.15 in. (3.8 mm.) and boronized 0.125 in. (3.2 mm.) copper were used. It was soon found that smaller wires were more sensitive to exposure for a short time at the lower ranges, and so a piece of 0.05 in. (1.3 mm.) wire of each kind was also used in each run. No accurate measurements of brittleness were made, as a simple bending test was sufficient for our purpose. If a wire would not stand bending to a right angle and back without cracking, it was termed brittle. Samples were run at 100° intervals from 400° C. to 1,000° C. and held for two hours.

EFFECT OF HYDROGEN.

Electrolytic hydrogen, purified by running over hot copper and thoroughly dried over P_2O_5, was used.

Commercial Copper.

At 400° C. no brittleness could be detected after a two hours' anneal. After 31 hours' anneal, however, a decided weakening had occurred.

At 500°C. the smaller wires were quite brittle after two hours, and the large one cracked on the surface, showing that the action had started.

At 600°C. the brittleness had penetrated about 3/64 inch (1.2 mm.) on the large piece, and the small wire was extremely brittle.

At 800°C. the large wire became so brittle that it broke on bending through an angle of 10°.

At 1000°C. the copper was still brittle, but showed a marked tendency toward recovery.

On remelting in hydrogen the copper was restored to its original ductility.

Deoxidized Copper.

Copper, which had been deoxidized by the addition of boron in the form of boron carbide, and run through the same treatment as the regular copper samples above, in no case exhibited the least trace of brittleness.

EFFECT OF WET HYDROGEN.

Hydrogen bubbled through water had the same effect as the purified hydrogen, except that the brittleness did not appear until a temperature of 600°C. was reached. Deoxidized copper was not affected at any temperature.

EFFECT OF CARBON MONOXIDE.

Brittleness was not observed in this treatment until a temperature of about 850 to 900°C. was attained. At 900°C. and 1000°C., however, extreme brittleness was caused in two hours. As in previous cases, boronized copper was unaffected. The high temperature needed to produce brittleness in this case was probably due to the presence of considerable CO_2 mixed with the CO. The CO gas was made by passing a slow stream of air over incandescent charcoal. The samples were all somewhat oxidized on the surface.

EFFECT OF CARBON DIOXIDE.

Tank CO_2 dried over sulphuric acid was used in these experiments. The samples scaled quite severely at the higher temperatures, but no perceptible brittleness occurred in any of the samples except the boronized copper run at 900° C. and 1000° C. This result was rather unexpected, and the reason why this deoxidized copper should be more brittle than the regular copper under these

particular circumstances is not yet clear, as oxidation should have made each one brittle.

EFFECT OF STEAM.

A slight brittleness was observed in regular copper at 700°C. This increased with the temperature, but in no case was the material as brittle as that treated in hydrogen or CO gas. An explosion of the hydrogen gas occurred at the mouth of the furnace running at 1000°C.

SUMMARY.

It has been shown that the brittleness of copper developed during heating in the process of manufacture and frequently ascribed to "burning," is in reality a deoxidation. With ordinary commercial copper, serious brittleness begins to appear at 400°C. in dry hydrogen, at 600°C. in wet hydrogen, at about 800 to 850°C. in CO, and at 700°C. in steam. Copper which had previously been deoxidized by the addition of boron remains unaffected at all temperatures in a reducing atmosphere. This brittleness is therefore due to the reduction of the cuprous oxide around the primary copper grains, leaving a spongy mass of little mechanical strength, and not to any direct action of the hydrogen upon the copper itself.

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DISCUSSION.

President Addicks: I have always been particularly interested in the properties of metallic copper. Some points in this paper I should take exception to, for example, the small quantity of cuprous oxide left in copper by the refiner is not to maintain physical properties but to prevent "spewing" or the sudden rejection of gases upon cooling, thereby making an imperfect casting. I once conducted a series of large-scale tests at a rolling mill on purposely defective wire bars, and could find no trouble in rolling

so-called overpoled bars as far as brittleness is concerned. There was a slight lowering of the electric conductivity, that was all. I suspect the ejected gases are largely carbon dioxide, which may have something to do with the brittleness of copper deoxidized by boron in certain of Mr. Ruder's experiments.

The value of the paper would be increased if we could have some analyses of the copper content of the sample wires. Is boronized copper truly deoxidized, that is, 99.99 percent copper?

The temperatures used are very high from an annealing standpoint. 500° C. should be sufficient to adequately soften copper quickly, though I do not know what may be required for calorizing. I should expect crystal growth has much to do with the weakness of the wires annealed at excessive temperatures, although the experiments show that the atmosphere plays a decided part. Wires annealed in the air by electric heating show a marked decrease in conductivity at high temperatures, due no doubt to direct absorption of oxygen, and I would therefore be inclined to ascribe the brittleness to an absorption of hydrogen rather than to a removal of oxygen. We know how brittle cathodes can be made when subjected to the influence of hydrogen during deposition.

W. E. Ruder: If the last statement by Mr. Addicks, that the brittleness was due to the absorption of hydrogen, was true, there is no reason why the deoxidized copper should not absorb the same amount of hydrogen as copper that is not specially deoxidized. Moreover the copper melted in hydrogen would then be brittle also.

Microscopic examination shows the location of the oxide in an envelope around the primary grains. This is not present in copper thoroughly deoxidized by poling or by fusion in hydrogen.

Dr. Lindsay tells me that arsenical copper does not show this brittleness so markedly on annealing in a reducing atmosphere, and the microscope shows that in this case the oxide is distributed differently than in normal copper. The oxide, in this case, is distributed in small areas and not confined to the grain boundaries.

J. W. Richards: Mr. Ruder's experiments are proof that the brittleness can not be due to hydrogen, and Mr. Addicks' statement that he has found overpoled copper bars not to be brittle does not

bear upon the point, because these overpoled bars have the copper oxide removed while the copper is in the melted state, and therefore there is no spongy reduced copper oxide in the specimens as there is in Mr. Ruder's specimen.

I think Mr. Ruder's conception of the films of copper oxide around the crystals of copper being reduced by the gases, and thereby causing brittleness, is a very probable explanation.

A paper read before the New York Section of the American Electrochemical Society, in Joint Session with the New York Sections of the American Chemical Society and the Society of Chemical Industry, on February 11, 1916. Called up for Discussion at the Twenty-ninth General Meeting of the Society, in Washington, D. C., April 27-29, 1916.

MAGNESIUM.

By Wm. M. Grosvenor.

The Element.

You all know the chemical position and character of magnesium, the leading member of the alkali earth division of the second group.

Uses.

Its chief uses are:

1. Scavenging alloys, *i.e.*, clearing up oxides of other metals and making far denser, cleaner, stronger and more homogeneous alloys. Valuable in aluminium, nickel, copper, brass, bronze, etc., and special steels, because of its intense avidity for both oxygen and nitrogen.

2. Alloying itself, with aluminium or aluminium containing traces of one or more of the other metals Cu Ni, Zn, Pb, Bi, Sb, Fe, etc. Greatly modifies their crystallization and physical properties; alloys readily with most metals and melts at a convenient heat.

3. Illumination, as in military uses for shrapnel trailers, star bombs, flare lights, etc., and in photography for flash lights. Its easy inflammability (about 800° C.), the high heat of combustion (134,000 cal.), the relatively low temperature of vaporization (1,100° C.), the intensely white oxide produced and the high temperature of volatilization of this oxide, are the essential factors of these uses.

Quantity Made, and Prices.

How much is used? Records of imports into the United States for the year prior to the present war indicated 38,000 lb. (17,000 kg.). About 100 lb. (45 kg.) a day, therefore, seemed to be a safe production to undertake. Prices before the war had

been very steady around $1.45 per lb. but it seemed reasonably certain the cost need not exceed $1.00 per pound, and after the war began the prices being paid for remnants of imported lots quickly rose to $2.50. Some of the first demands here were from wholly unexpected quarters, in surprising amounts and at amazing prices. The most urgent, almost pitiful demands, came from quarters that were not even suspected to be interested. One consumer has contracted for 24,000 pounds; another 15,000, these two alone taking for strictly domestic use more than was supposed to be the total importation. There are at least three other buyers of similar quantities, but exact amounts are not yet established by yearly contract, and even at present prices the yearly consumption for strictly domestic use is about 50 tons. A great deal of the material is being imported under other names and most carefully disguised—secrecy being preferred to economy. Prices as high as $10.00 per pound were gladly paid at first for the domestic product. For some months then the prices jumped around from $5.00 to $7.50; now, however, for a number of months the price has been practically fixed at 5.50 per lb. of "guaranteed 99 percent," actually about 99.5 percent.

In spite of the beautiful appearance of the German bars they rarely exceeded 98 percent magnesium, and often fell as low as 96 percent. The process of extrusion of the bars concealed impurities by drawing them out into minute threads. It is safe to say that the regular commercial grade of metal made here now is superior to anything ever imported.

Reasons for these Prices.

It may seem ridiculous to ask or pay such prices. Let us consider. The alloy market constitutes the bulk of the business, and governs prices. In aluminium castings for instance about less than 2 percent of magnesium cleans the metal and leaves ¾ to 1½ percent in the casting, about doubling its tensile strength, and quadrupling its resistance to shock or jar. It reduces the cost of machining more than 50 percent, halving the number of resets on the cutting tool, giving clean-cut machine surfaces, and permitting a polish to be secured with the last cut instead of a separate operation. With care, 1½ percent of magnesium, at $5.50 per lb., is all that is needed, *i.e.*, 8¼ cents per pound of

casting actually required to do the same work. The increase in strength means, in some cases, a reduction in weight of casting of 50 percent; it is generally not less than 25 percent. This is a great saving even at normal prices of aluminium, since it amounts to about ¼ of 20 cents, or 5 cents. With aluminium at 60 cents it amounts to 15 cents worth of aluminium saved, for a stronger and more stable mechanical result. The saving in machine work alone when the casting requires much machine work more than pays for the use of magnesium. So much for the consumer or user. Now the manufacturer of Mg. has certain considerations (of necessity rather than mere excuse) for the high prices. Cost of production abroad prior to the war approximated $1.00 per lb. Sales in England were about $1.30 and here about $1.45 per lb. At that time $MgCl_2.6H_2O$ was selling for about $18 per ton. Present prices here are now about $60, nearly four times normal. Other chemicals used in the manufacture have increased to ten times their normal price. One other factor, *i.e.,* insurance, must be considered in two forms. First, the insurance against cut prices and dumping that may come immediately upon the close of the war, making the plant and market development work absolutely worthless. Second, the insurance against partisan interference. As a matter of fact, in the case of two plants not a pound of material from either of which has gone for foreign military purposes so far as we know, there have been repeated efforts at molestation and some serious interruptions.

In considering prices it is well to mention separately export prices. Before the war nearly all the magnesium for England, as well as the United States and France, came from Germany. Since the war both France and England are producing in considerable quantities of excellent purity. This fact, and the failure abroad to realize the strenuous conditions here, account for the unwillingness of buyers abroad to pay more than $3.50 per lb. for powdered metal (all the above-named prices were ingot or bar).

Present Production.

At present there is being produced at two points in the United States about all the present alloy market will absorb, and an increase of plant is being made of about 25 percent of the present

capacity. One other producer makes only about his own requirements. Two others are soliciting business but have failed to fill orders—in one case the order is now over a year old and still stands unfilled. All told, we believe the present production is at the rate of something over a million dollars' worth a year and will be slightly in excess of the present domestic needs.

Possibilities.

The use of the metal for scavenging purposes depends on price of metal compared with price of material to be scavenged. For use with copper, brass, bronze, etc., the magnesium can be used at far higher prices than for steel. But the big consumption of the material can only come when it directly replaces aluminium as the predominant metal in the alloy, and arrives at a correspondingly low price. It makes beautiful castings, machines easily and well, is about a third lighter than aluminium, and can be made about two to four times as strong. The coefficient of expansion reported is practically the same as aluminium. When properly pure (over 99.5 percent), it is apparently quite as resistant to corrosion as aluminium, equal if not superior in electrical conductivity (about half that of copper), and superior in heat conductivity (also about half that of copper).

Processes.

1st. Reduction of fused $MgCl_2$ by Na.
2d. Electrolysis of the fused double chloride, usually $MgCl_2.KCl_2$.
3d. Reduction by carbon (patented).
4th. Electrolysis of dissolved MgO (applied for).
5th. Reduction of fused $MgCl_2$ by aluminium (applied for).
6th. Reduction of oxide or carbonate to slag-forming residues (applied for).
And some others.

The first process involves the production of metallic sodium, and we have been using the Castner process for this purpose to satisfy ourselves just what the sodium would cost and what the possibilities in this direction were. Existing conditions, the demand for sodium and sodium peroxid, forbid its consideration with a minimum of about two lb. of Na consumed for every lb.

of Mg produced, and the necessity of producing dehydrated fused $MgCl_2$ to start with.

The second process has been perfected and is very largely used abroad. We have commercially used and studied the process here and, with the cheapest water power and chloride, prices under normal conditions by this process must rule above $1.00 per lb.

The third process, reduction by carbon, is absolutely fascinating in its possibilities. The product is a black or gray powder. Believing such a product would be valuable, the manufacture was carried out on a scale of about 25 lb. (11 kg.) per hr. As the difficulty of selling the product became apparent, much time and effort were devoted to attempts to recover the metal in fairly pure form. Owing to serious objection both on the side of cost and regularity of product this process was superseded.

The other processes will be discussed on some other occasion when the engineering problems they involve are believed to be finally solved in the best way, and the patent office has finished considering them. The chemical side of each has been thoroughly worked out, however, so that some conclusions may be drawn from the large laboratory or small commercial operations. These may be of considerable interest.

At least one of the processes appears to be adapted to produce directly metal averaging 99.6 percent purity, in tons per day instead of pounds. Laboratory tests give a raw material cost of 4 cents per lb. of magnesium, and indicate a fuel cost which approaches 3 cents as a theoretical limit, though the practical figure will probably be several times as high. The final selection of various possible engineering means and methods remains to be worked out, but it scarcely seems possible that either labor or repairs should exceed 2 cents per lb. Thus if commercial yields maintain the experimental level, and three times the theoretical power is commercially required, we have prospects of a net factory operation cost (without interest, amortization, insurance, patent, administration or selling) of 17 cents per lb. If only 75 percent yield is obtained, this net factory cost would be about 22 cents or a total cost with all overhead expenses of 35 cents and a selling price of 40 cents to 50 cents, according to tonnage.

It may seem premature to speak of such possible prices in view

of present conditions. It is only the present price of $5.50 that justifies or even makes possible the thousand and ten thousand dollar experiments that have been tried and must be tried again and perhaps again during the next three to five years, before the tide turns. The men who are doing this work do not cultivate talkativeness as a preference. Just at this time, however, certain consideration of public welfare should take precedence of preference.

Therefore, at the risk of criticism and possible financial sacrifice it seems to be a duty at this time to point out what may possibly be expected of magnesium. Few realize the extent to which it is valuable in military work. One of the great foreign explosive experts stated that he would be glad to pay $1.50 per lb. for 500 tons. A single contract for shrapnel being executed in this country would require about fifty tons. The illuminating bombs to make daylight over the enemies' works and trenches consume large quantities. The trailer attached to shells serves at night to show the effectiveness of the fire. For all these purposes magnesium produces a result that cannot be approached by antimony or aluminium. Consider what it means to aeroplane, dirigible, and motor construction, to high-speed engines of every type, to reduce weight one-third and double strength, to have a material that has a density of 1.75 and may be hot rolled to 35,000 lb. per sq. in. (25 kg. per sq. mm.) or cold rolled very much higher.

DISCUSSION.

President Addicks: I remember at school one of the rules in the debating society was to admit all you safely can, and I think that this paper is a most creditable example of that rule. A great deal of information is here put forward a year or so earlier than most people are willing to do it. We must not expect to know the whole story. I think Dr. Grosvenor is to be congratulated on the advanced stand he has taken in this matter.

There is a question which occurs to me, which some one may be able to answer, and that is this: Does magnesium have sufficient

energy of combustion to make it a fire risk in the massive state, or only in the finely divided state?

F. A. J. FitzGerald: I have made inquiries in regard to the question Mr. Addicks asks and was told by an experimenter that he had found magnesium alloyed with a very small amount of aluminum is perfectly safe. Whether or not he ever tried any experiments with pure magnesium I do not know, but with the aluminum alloy there was not the slightest danger of fire.

G. A. Roush: I should say that in the case of ordinary alloys for aviation purposes and similar uses, containing a considerable percentage of other metals, there would not be any possibility of a fire hazard. The pure metal itself in massive sticks would present, of course, a certain danger. It is not anything at all like the danger which would be presented by the finely divided material.

President Addicks: Will it support combustion?

G. A. Roush: It will, of course, if it is heated up in mass to a sufficient temperature; but it is a very good conductor of heat, and this makes it difficult to ignite it by the local application of heat to a large bar of the metal. On the other hand it is a very simple matter to light a piece of magnesium ribbon or a pile of magnesium powder with a match, because the conditions are such that the heat conductivity of the material is reduced in the first case by the small cross section of metal and in the second by the fine state of division, thus allowing the metal to be heated locally to the ignition temperature, and then the combustion proceeds until the entire mass is consumed.

W. M. Grosvenor (*Communicated*): In the massive form magnesium is practically no more inflammable than aluminum. The melting point is not far from that of aluminum. The ignition point not much lower if any and the heat conductivity about the same. Theoretically one would not expect any greater fire risk. Practically, a quarter-inch bar of magnesium can be held in the flame of a blast lamp until it becomes red hot, coats itself with a surprisingly thin covering of oxide and finally melts and drops off without setting fire to the rod.

A paper presented at a Joint Meeting of the New York Sections of the American Electrochemical Society, American Chemical Society, and Society of Chemical Industry, February 11, 1916. Called up for discussion at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

LIQUID CHLORINE.

By G. Ornstein.

You are all familiar with the element Chlorine, its history, manufacture and characteristics, so that it will be hardly necessary to go into great detail on this subject.

The first process employed commercially was the same which we have all used as students in the laboratory—namely; that of generating it from manganese oxide and acid, which may be either muriatic or a mixture of salt and sulphuric acid. This process later on was made eminently practical by Weldon's invention of recovering the manganese oxide by means of addition of lime to the waste liquor, blowing air through the mixture and returning it in this regenerated form to the process. This Weldon process is the only purely chemical process, operated on a commercial scale, which furnishes a chlorine gas of sufficient concentration to be used for liquefaction. The Deacon process, in which hydrochloric acid fumes are decomposed in the presence of air and a contact substance, such as copper chloride, gives a diluted gas, and therefore is not practicable for the purpose of liquefaction, at least not directly.

To overcome this drawback, in this and other instances where a weak chlorine gas is obtained, several processes protected by patents have been worked out, particularly by Goldschmidt and Sperry, which aim at absorbing the chlorine from a weak mixture, the former by stannic chloride, the latter in the form of chlorine hydrate, thus separating it from the diluting impurities, and later on decomposing it again by application of heat, for the purpose of producing pure chlorine. In the Acker process, in which an extremely poor gas was obtained, one even went so far as to first convert the chlorine into bleaching powder and to subsequently decompose it by acid.

However, it seems that none of the chemical processes are

operated at present for the purpose of liquefaction, except perhaps in a few individual instances, and the chlorine liquefied nowadays, here as well as abroad, is almost entirely produced by electrolytic processes.

The electrolytic decomposition of brine, or potassium chloride, is known to you in principle. It consists in passing an electric current of high amperage through an electrolytic cell, in which the anode is made of carbon, or, what is much to be preferred, Acheson graphite, or fused iron oxide, and the cathode of iron, either in the form of a perforated sheet, wire screen, or in some instances a solid sheet, depending on the details of construction.

When the electric current is passed through the cell, the brine is split up into its components, chlorine which escapes at the anode, and caustic soda or caustic potash at the cathode. The products of the electrolysis have to be kept apart, as otherwise they will combine again forming hypochlorite and eventually chlorates, and quite a number of different forms of apparatus have been made and patented to prevent this re-combination. In the majority of cases, diaphragms of various designs are employed (for instance, in the Gibbs, Townsend, McDonald and Billiter cells) the basis of which is mostly asbestos. In others they are kept apart by gravity and by causing a constant flow of liquid in the direction from the anode to the cathode. This principle is employed in the Bell process and others.

A third principle is employed in the mercury cell, in which the cathode is mercury instead of iron, absorbing the sodium or potassium under the influence of the electric current, and this in turn is released again by water, outside of the electrolytic cell, in the form of caustic. The pure mercury is then again returned to the cell and reloaded at the cathode, but no matter what the construction of the cell may be, in all instances a highly concentrated chlorine can be obtained which, with graphite or iron oxide anodes, which are less subject to electrolytic oxidization than carbon, should easily yield gas of 97 to 98 percent purity, the balance being carbon dioxide, electrolytic oxygen and a slight trace of air. With iron oxide electrodes no carbon dioxide can be formed, but the amount of electrolytic oxygen will be correspondingly higher. However, only in a few cells is a gas of this purity actually obtained, on account of mechanical defects, such as leaks in

the cell covers, or pipe lines, or through negligence of the cell attendants.

For the liquefaction of chlorine it is of great importance that attention should be paid to generating highly concentrated gas, because otherwise the percentage which can be liquefied from a certain volume of chlorine will decrease rapidly with each percent of impurities. The following curves illustrate the influence of concentration as well as of pressure and temperature. For the

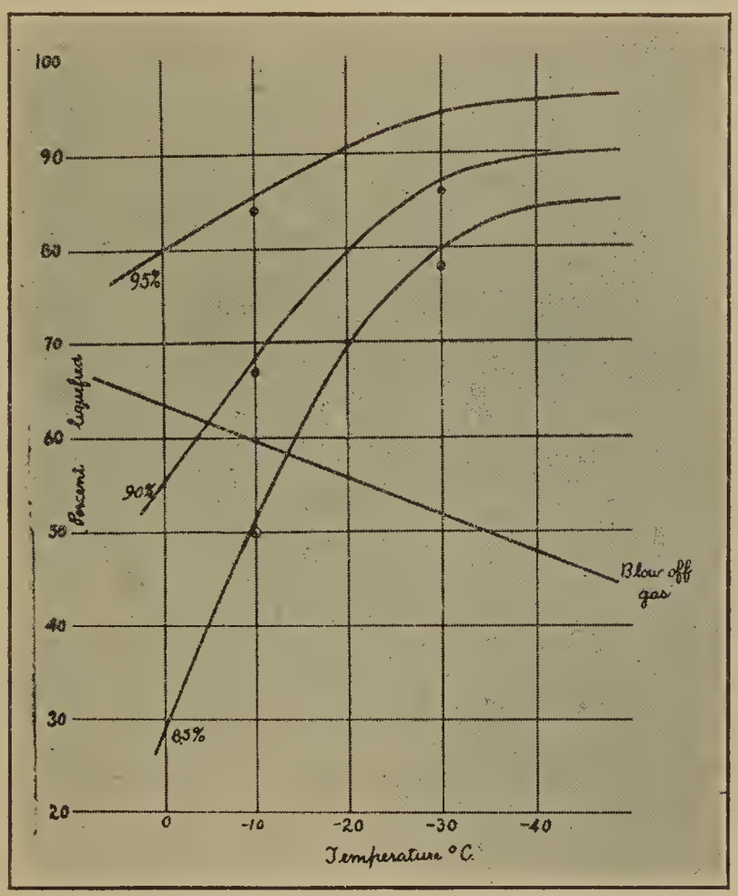

Fig. 1. Influence of temperature on liquefaction.

figures on which these curves are based I am indebted to our works manager, Mr. Neuhaus.

The unliquefied residue, which still contains between 55 and 65 percent of chlorine, is called blow-off gas and is released from the liquefying machinery, from time to time, when the pressure exceeds certain limits. It is generally conveyed to the bleach chambers, which is the preferred way of both using and getting rid of it, as on account of its dilution it can be used only for a limited number of other purposes. In any case, absorption capac-

ity of some kind has to be provided, and it therefore appears that a chlorine liquefaction plant can be operated to advantage only in connection with the manufacture of other chlorine products.

There have been a great many attempts to liquefy chlorine, ever since the beginning of the nineteenth century, but until recently they were largely confined to laboratory experiments of no practical value. The first liquid chlorine was obtained in 1805 by

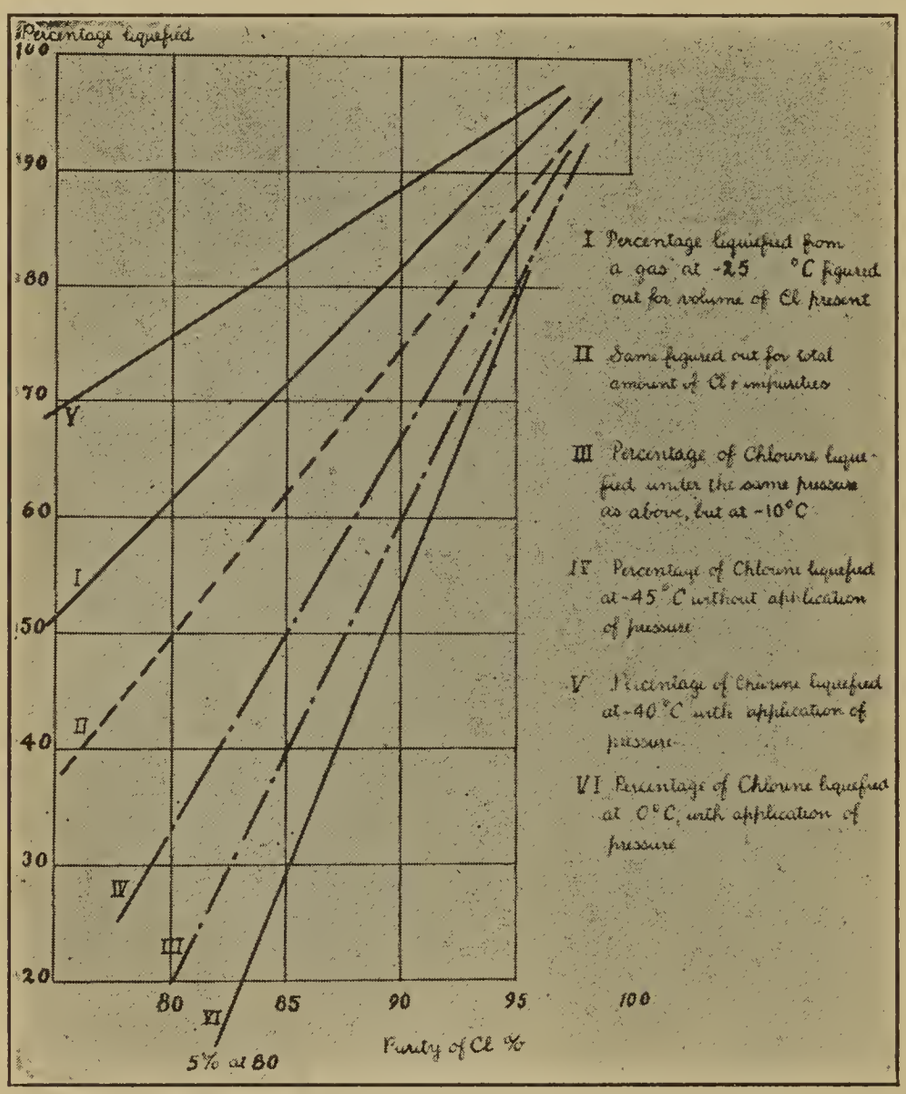

FIG. 2. Influence of pressure on liquefaction.

Northmore, and as early as 1823 Faraday demonstrated the well known experiment which you find in every text book—namely, the decomposition of chlorine hydrate in a sealed and bent glass tube in which the hydrate is heated in one branch of the tube and the escaping chlorine liquefied in the other one, which is cooled down in a freezing mixture. But until after 1880 nothing was done towards working out a commercial process.

Between 1880 and 1890 a number of processes were worked out which at least made an attempt to produce liquid chlorine on a commercial scale. For instance, Vautin attempted to compress chlorine gas by pumping air into tanks containing chlorine and at the same time cooling it down to a low temperature. Others, Hannay and Marx, for instance, based their processes on the decomposition of chlorine hydrate in a closed vessel. Heinzerling first compressed chlorine, cooling it to a low temperature, and then liquefied it by sudden expansion. None of these were successful, and commercial liquid chlorine remained an unrealized dream until the arrival of the process of Knietsch, of the Badische Co., who in 1888 placed the first liquid chlorine on the market. He

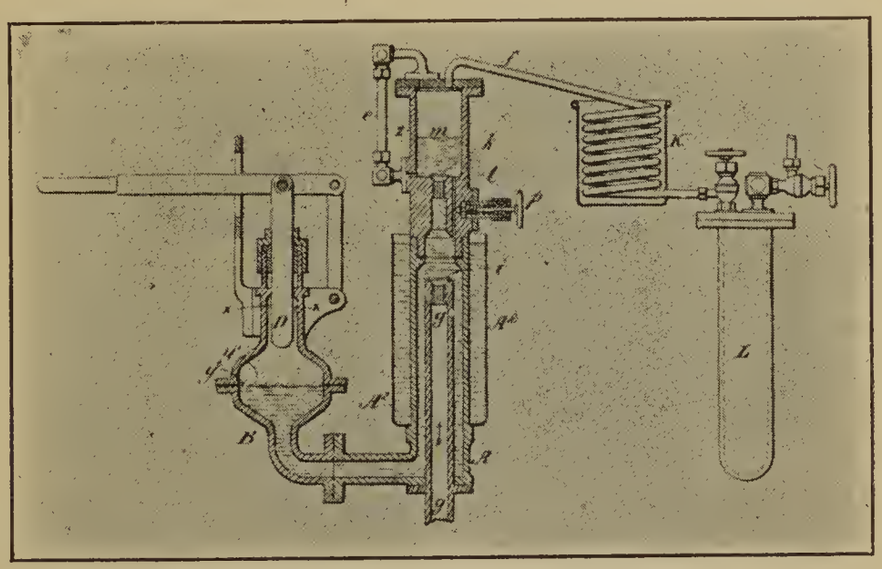

Fig. 3. Knietsch liquid piston.

was the first to realize as being of fundamental importance that for commercial liquefaction a chlorine had to be used which was both highly concentrated and free from moisture, two points which the above-mentioned inventors had overlooked. He also found that chlorine carefully dried did not attack iron or a number of other metals employed for building commercial machinery, and through an ingenious device of a so-called liquid piston, which is illustrated on the accompanying figure, he was able to put the chlorine under a high pressure without any danger of leaks through the stuffing box around the piston, causing corrosion, etc. The liquid media which he applied consisted of a column of petroleum around the piston and under this and in the other branch of the

U-shaped cylinder he used concentrated sulphuric acid. The liquid piston was lifted up and down by a plunger moving in the petroleum and thus sucked in and compressed chlorine gas, which through a separator was carried on to a condenser where under the influence of low temperature it liquefied and was then filled into the shipping containers. He also heated the sulphuric acid by a steam or hot-water jacket, in order to reduce the absorptive power of the acid for chlorine gas.

According to my knowledge, most processes which are now in operation are still based on this fundamental principle; namely, all of them are using a liquid for compression; and while they may have been simplified in some way, for instance by omitting the petroleum and not heating the sulphuric acid, or by making changes in other directions, compressing the chlorine by entrainment, or in two- or three-stage compression, yet in almost every case the principle has been maintained.

There are several processes on the market, for instance that of the Linde Co. of Germany, by which liquefaction is effected simply by cooling to —45°C. or lower, without any pressure, but the drawback of this process is that the percentage liquefied is lower throughout than that obtained with the combined system of compressing and cooling, as has been illustrated by the curves shown previously.

Regarding the relative merits of the various processes I must hesitate to express an opinion. There is so much secrecy observed in this field, as in all lines of chemical industry, that I do not know enough about the details of construction and operation used by most of the other manufacturers to warrant my passing comparative criticism on this subject.

In one point I feel that "the people who know" will agree with me; stick to what you have got and tried out in the course of years and of which you have studied all the little knacks and moods, and never mind what excellent results the other fellow "says" he gets. I would rather hunt for trouble in a 12-cylinder automobile motor than tackle a chlorine compressor when it is in the mood of the "morning after the night before."

The chlorine is shipped in steel cylinders, containing about 100 pounds (45 kg.) net, weighing empty 70 to 100 pounds (32 to 45 kg.) For large quantities it is also shipped in tank cars. The

pressure in these containers varies with the temperature, but will drop rapidly on account of the heat absorbed by the evaporation if chlorine is drawn off continuously, even in relatively small quantities. In one place where chlorine was drawn off continuously for the purpose of water sterilization at a room temperature of about 2°C. the pressure dropped in 24 hours from around 55 to 15 lb. per sq. in. (3.7 to 1 kg. per sq. cm.), although not more than ¾ lb. (0.35 kg.) per hour was taken from a set of 4 cylinders. This cooling or freezing action can be easily counteracted by playing steam on the cylinder until the frost which will form has disappeared, placing it in a tub with warm water, or in a cabinet which is kept warm by artificial heat, or other similar means.

Liquid chlorine was unknown in the United States until the year 1909. Prior to this date quantities of liquid chlorine had been imported from Germany, but these were used solely for experimental purposes on a more or less extensive scale, but the United States did not begin any manufacture until the year above mentioned. It was in the beginning of this year that the Electro-Bleaching Gas Company, after about two years of experimenting,[1] erected its first compressors, and a short while later two more chlorine concerns started in operation: the Goldschmidt Detinning Company and the Castner Electrolytic Alkali Co. The Goldschmidt Company used the product largely for their own purposes, namely, the detinning of tin scrap, whereas the Electro-Bleaching Gas Company had to find and build up a market for this entirely new product.

The two most important fields to which the liquid chlorine was to be introduced were the bleaching of vegetable fibre, such as cotton, flax, and paper pulp, and chlorination of all kinds, such as of ores, organic compounds, pharmaceutical products, etc. Most of all, it was necessary to instruct our purchasers how to use it for their various purposes, and we still recall with considerable pleasure the many comical occurrences which happened at that time. In one textile mill they apparently thought the cylinder contained something like a liquid bleaching powder, which they had been accustomed to use for generations. So they simply attached a hose to the valve outlet and tried to empty the cylinder into a vat containing water for diluting to proper

[1] Carried out successfully under the direction of Dr. B. C. Hesse.

strength. The result can be easily imagined. After a minute or two there was nobody left in the mill who could be induced to enter the place and shut off the valve, and the letter we received was anything but complimentary; many other episodes of a similar nature occurred.

Therefore, before we could market the product we had to instruct our purchasers how to use it, and we were compelled to make demonstrations of how to prepare the bleach liquor and how to bleach yarn with it, in one mill after the other, until finally we succeeded in convincing a number of the largest and most conservative mills of the decided advantages of liquid chlorine as compared with bleaching powder; for the past four or five years they have definitely abandoned the latter in favor of the former.

At the beginning we had to convince many chemists that the amount of available chlorine present in a bleaching solution prepared with liquid chlorine and alkali, such as soda ash, was equal to the full amount of chlorine passed in. They based their objections on the equation:

$$Na_2CO_3 + Cl_2 + H_2O = NaCl + HOCl + NaHCO_3,$$

or if caustic soda was used:

$$2NaOH + Cl_2 = NaOCl + NaCl,$$

and insisted that these proved that one-half of the chlorine was converted into NaCl and thus wasted for bleaching purposes.

The assumption was that in bleaching powder the available chlorine was present in the form of $CaOCl_2$, which as a matter of fact is the usually accepted formula for the powder, thus giving the impression that all the chlorine present was in the available form. But upon dissolving this will be split up according to:

$$2CaOCl_2 = CaCl_2 + Ca(OCl)_2$$

so that one-half of the chlorine is converted into available chlorine and the titration with As_2O_3 proceeds according to the formula:

$$Ca(OCl)_2 + As_2O_3 = As_2O_5 + CaCl_2.$$

Thus it can be seen that the so-called "available chlorine" does not represent the actual amount of chlorine present in the hypo-

chlorite but only half of it, and is rather an expression for the available *oxygen* in the same compound, which, if expressed in chlorine value must, on account of the bivalency of the oxygen and the monovalency of the chlorine, naturally be twice as high.

It follows now, by comparing the above equations, that the chemical reactions of both bleaching powder solutions and those made with liquid chlorine and alkali are identical and the fact can be no longer astonishing that by using liquid chlorine for the manufacture of bleaching solution an available chlorine content is obtained substantially equal to the number of pounds of chlorine absorbed by the solution.

We were able to show, and in connection with this wish to acknowledge the valuable assistance rendered us by Dr. J. M. Matthews, that bleach solution thus prepared gave decidedly better results than bleaching powder. We could demonstrate that only one-half of the amount of available chlorine, and even less, is required to be present in order to give the full bleaching results which formerly had been obtained with chloride of lime, and the tensile strength of the goods was correspondingly improved.

A large reduction of the so-called "sour," that is, the use of weak sulphuric or muriatic acid after the bleaching bath for destroying the last traces of residual chlorine, also served to improve the strength. The explanation for its increased efficiency seems to be that in case a bleach is used in which the chlorine has been combined with soda ash, the presence of free hypochlorous acid causes a more rapid and more efficient action on the fibre than the neutral calcium hypochlorite. In addition, any bleach prepared with soda as a basis and with entire absence of lime salts seems to have a higher penetrating power on the cloth on account of no substances being present which are capable of forming insoluble precipitates on the fibre, a theory which is substantiated by the observation that a hard twisted yarn or cloth requires less available chlorine, as compared with the necessary quantity of bleaching powder solution, than a material of a looser texture.

Another large field in which liquid chlorine is now used extensively is for chemical chlorination processes, in which the quantities consumed are not large enough for warranting a concern

to build a branch factory near the chlorine-producing plant for receiving the gas directly from the cells, and in which instance, therefore, liquid chlorine, being easily transportable, is the only other choice.

A number of manufacturers have tried to make the chlorine themselves from either bleaching powder and acid or manganese oxide and acid, but in most instances they have found that it was much more to their advantage to purchase liquid chlorine ready made; because in addition to the cost of the raw materials, which in either case exceed that for which liquid chlorine can be purchased, the latter has the advantages of being absolutely dry, chemically pure and under a pressure so high that it may be

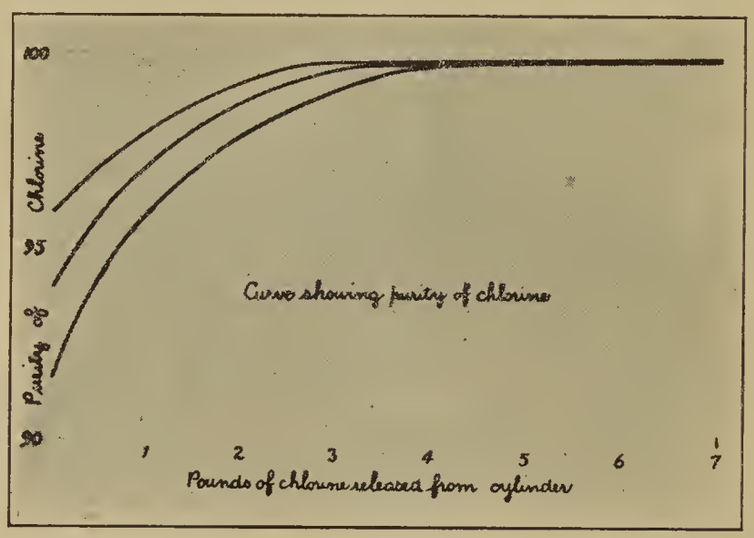

FIG. 4. Purity of chlorine.

easily conveyed to any point of application and forced through liquids to be treated without the troublesome medium of blowers, fans, pumps, etc.

The valve of the chlorine cylinder, also, permits of an easy and accurate regulation, whereas the above mentioned chemical processes after being once started cannot be regulated at will unless a gas meter is used in connection with them, which only introduces another source of trouble, because as the only sealing medium concentrated sulphuric acid must be employed.

Of the advantages just cited, its purity is one of the most conspicuous characteristics of liquid chlorine. When a fresh cylinder is opened it will usually yield at once a gas which is 96 to 98 percent pure, and after several pounds, from 3 to 5, have been

taken out it goes up to 99 percent and after another pound or two it will be at 99.7 and 99.98 per cent, and will stay there until the last drop of liquid has evaporated from the cylinder. With these figures, which can be easily substantiated at any time, liquid chlorine may justly be called one of the purest, if not *the* purest, chemical on the market. The initial slight amounts of impurities represent the small traces of air, etc., which were in the gas coming from the cells.

A third large field for the use of liquid chlorine has been opened up during the last three years, namely, its use for the sterilization of city water supplies and sewage. In this field as well as in the bleaching industry liquid chlorine had to fight again its old competitors, bleaching powder, and we are proud to say it made a pretty good showing even without making allowance for its youth and lack of experience.

After some experimental work had been done, the first commercial machines were installed in the Western New York Water Co. plant at Niagara Falls, N. Y., in November, 1912, where we received valuable assistance from Mr. F. H. Huy, general manager of the plants, and in Wilmington, Del., in January, 1913, where they are still in continuous satisfactory operation. They are based on the principle of absorbing a measured quantity of chlorine in a small amount of water, and subsequently adding this solution to the water to be treated. This so-called absorption process has the advantage of an even and rapid distribution of the sterilizing agent throughout the whole body of water, an advantage which is particularly apparent in large installations such as the Torresdale filter plant in Philadelphia, in which from 220 to 330 million gallons (1 to 1.5 million cubic meters) of water is filtered daily.

It is, furthermore, of advantage in plants in which the water to be treated is under high pressure, which in some places exceeds the pressure of the liquid chlorine itself. In these installations the application of the chlorine in the form of a solution which is forced into the main by means of a specially constructed pump is the only form in which the problem can be solved.

In the field of water sterilization the Leavitt-Jackson Engineering Co.'s apparatus is deserving of particular mention on account of the original principle involved, which consists in feeding the

chlorine into the water by weight, by a balanced beam construction acting on the chlorine feed valve, an excellent construction mechanically but not sensitive enough for the minute quantities of chlorine which are required by the large majority of water

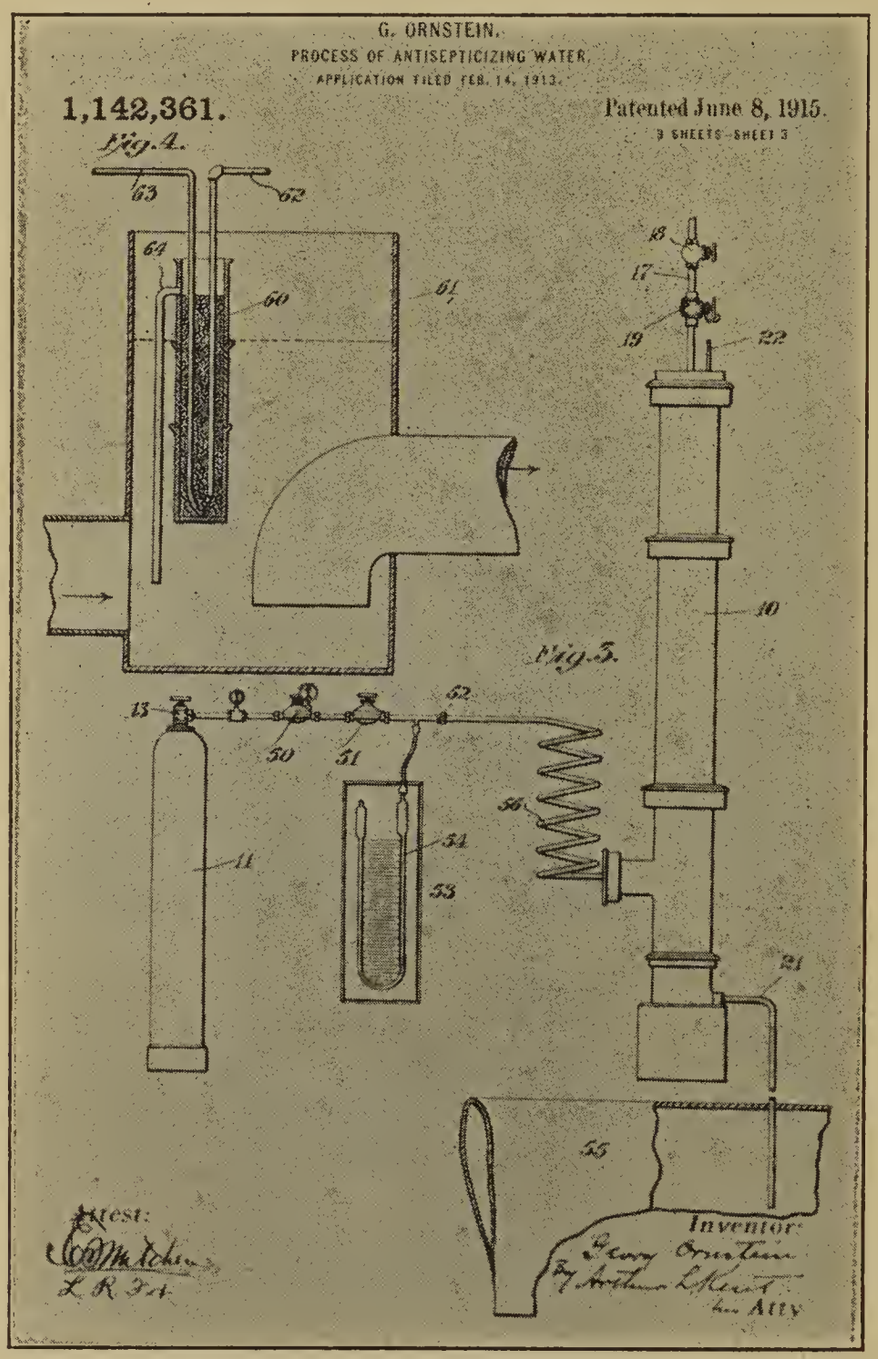

FIG. 5. Ornstein apparatus for sterilizing water.

works. The principle used in our first machine comprises the pressure regulation by a reducing valve or by two switched in series, the measuring of the rate of flow by the pressure difference caused by it on both sides of a calibrated orifice, and a sub-

sequent absorption of this measured quantity in water prior to its addition to the main flow of water.

Under the conditions shown in the figure, where the chlorine in the absorption tower is discharged against atmospheric pressure, it is unnecessary to connect the U-tube to the down-stream side of the orifice, as would have to be done were the chlorine to be discharged against pressures higher than atmospheric. We are also using a "rate of flow" meter for measuring the chlorine. Through constructions along these lines it has been possible to effect an accurate regulation of chlorine gas to any quantity as small as 1/40 ounce (0.7 g.) per hour and as high as 25 pounds (11 kg.) per hour, irrespective of any variations of the pressure in the cylinder, which in the course of operation may drop from 100 to 15 pounds (7 to 1 atmospheres) without influencing the rate of feed.

To thoroughly realize the importance of employing a sterilizing agent which can be added under perfect control as to its quantity, it is sufficient to point out the necessity of adding it to a continuously flowing stream of water, and that it has to be mixed and intermingled with it continuously, thoroughly and evenly. This is not possible with chloride of lime, because the devices used for this purpose, such as orifice boxes, etc., will after a short time be partly or entirely plugged up by a lime deposit and be in full working order only for a few days at a time. We have also succeeded in developing apparatus capable of automatically varying the amount of chlorine added in proportion to the rate of water flowing.

Further advantages which may be cited in favor of liquid chlorine are: absence of taste and odor in limits very much wider than those prevailing for bleaching powder, no sludge or dust, smell or other nuisance, and particularly its *efficiency,* which is 2 to 3½ times as high as the same amount of available chlorine present in bleaching powder, or in other words, one pound of liquid chlorine has approximately the efficiency of 6 to 10 pounds of chloride of lime.

In these various directions we had first to overcome considerable prejudice on the part of the communities, particularly as regards taste and odor. To what extent prejudice may sometimes run away with the common sense of the people may best be

learned from the fact that complaints about chlorine taste and odor came pouring into the office of the Board of Health in Buffalo four weeks *before* our machines were installed.

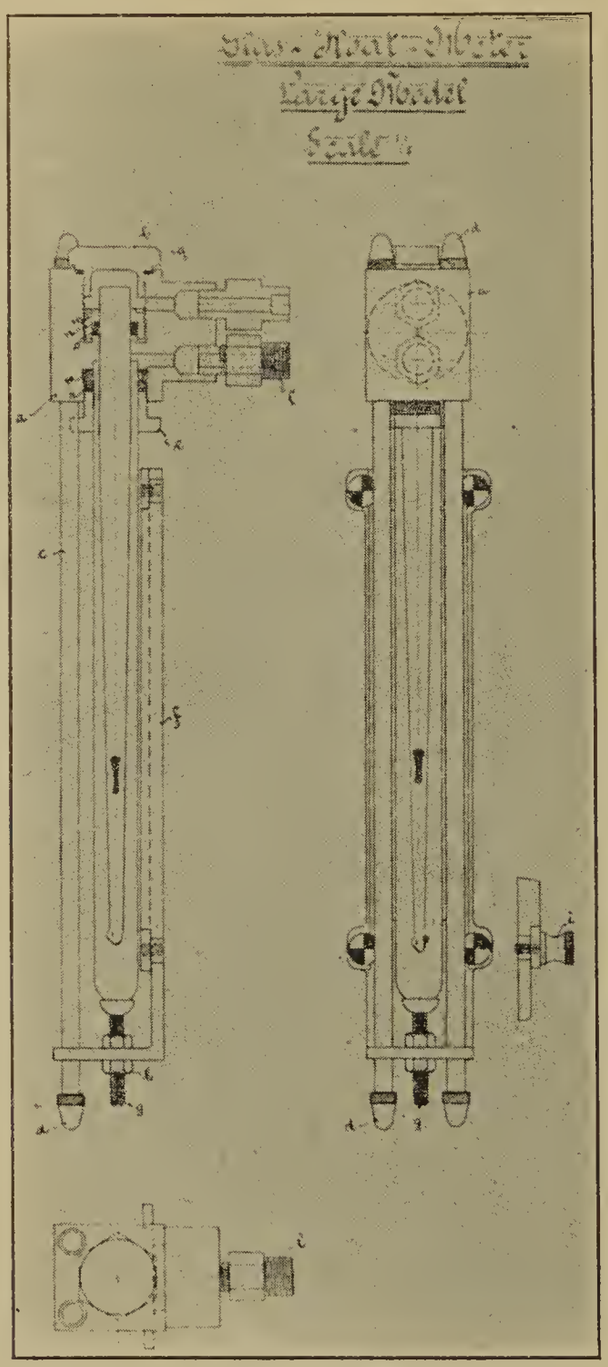

FIG. 6. "Rate of flow" meter.

The results obtained by this process and applied by these machines have been highly satisfactory, as can be gathered from the Board of Health records of the various communities. Cities which formerly had an exceedingly bad record for typhoid fever are now reported as being almost or entirely free from it, and in no

case whenever typhoid fever occurred in a community has it been possible to trace these back to the water used, but the reasons were always found in causes other than the city water supplies, such as milk, impure food, etc.

The war has naturally had considerable influence on the liquid chlorine trade, though the causes are entirely different from those which are responsible for the demoralization of prices of other chemicals. For the latter, the present situation is caused simply by the fact that these chemicals were hitherto imported from abroad and only small quantities, if any, manufactured here. Now the supplies being entirely shut off, prices, of course, have gone sky-high. Liquid chlorine, on the other hand, is an entirely domestic material which, therefore, could not be influenced by the shutting off of imports as to the quantity available. The increase in the trade and the price of liquid chlorine must principally be traced back to the shortage of bleaching powder, of which formerly more than 50 percent was imported, and on account of its being shut off its price has risen from about $23 per ton to figures between $200 and $300, whereas the price of liquid chlorine has only increased from $160 to $200 per ton to $240-$300. Taken in figures of available chlorine, which is the standard by which, apart from other considerations, the comparative values of the two materials are measured, this is now worth in bleach containing 35 percent available chlorine $570-$860 per ton.

How long these conditions will continue to prevail is hard to say. Several of the big manufacturers are enlarging their plants and their bleach capacity, which may to some extent relieve the present shortage, but scarcely enough to reduce prices to anywhere near normal. The enlargement of plants, however alluring, is carried out very conservatively, realizing that after reestablishment of peace imports will begin again from Europe, particularly from Germany and England, perhaps not immediately, as some assume, but soon after. In the meantime the price of liquid chlorine may still travel a long way upward before approaching the present value of available chlorine in bleaching powder. Owing to this condition, manufacturers have been much tempted to divert part of the chlorine from the liquefying machinery into the bleach chambers, and a certain stringency may

have been caused by this as well as by the exportation of moderate quantities for war purposes.

From the reports we have received from the other side of the Atlantic, liquid chlorine as such has been used as a weapon for incapacitating the enemy. To what extent these reports are strictly true and what part liquid chlorine as such has played in it, we do not know. I have read only one report, in one of the medical journals, which seems to be entirely unbiased and therefore in fair accordance with the facts, free from newspaper sensationalism and similar causes for one-sided treatment of the case. The report mentions more or less severe affections of the breathing organs, so severe in some instances that it seems incredible, according to my experience, that they should have been caused by inhaling of chlorine gas. Of course, I do not doubt that chlorine can be very detrimental to the human system in a closed room, from which there is no escape, but in the open air with a wind blowing, no matter how gently, it seems next to impossible that any suffering beyond that of temporary coughing spells, vomiting, etc., could possibly be caused.

It has been suggested from various sides, and it is undoubtedly a fact, that the chlorine, if employed, is mixed with other ingredients, such as bromine, sulphur and others, which would cause more severe and more lasting irritations than chlorine alone. I know personally of one instance in which sulphur has been used in connection with liquid chlorine.

We naturally have had a long experience in this line, particularly at the start when we had to struggle with a good many imperfections, leaks, etc., and never in any instance have we seen any lasting detriment suffered by any of our men. I have also had several years' experience in Germany along the very same lines, and there also have never been able to observe one single case of this kind. To appreciate this statement fully you ought to see into what kinds of atmosphere our men had to go sometimes without using any protection whatsoever, and when they had swallowed half of our production and were coughing violently they took a drink of Rexall's A. B. C. seltzer or bromoseltzer, and a few minutes later were back in the plant. These compounds, as well as any other of a stimulating or nerve-relaxing influence, seem to be the best antidote for chlorine, among

them a good stiff drink of whisky. If these are not available, inhaling of alcohol, chloroform or tetrachloride of carbon vapors spread out on a handkerchief will give speedy relief, but with the two latter ones one should be careful that no narcotic effect takes place. The inhaling of ammonia, which is recommended in several text-books, should be absolutely rejected, because in most instances the irritation grows only worse instead of better.

Prevention is better than cure, and the best prevention of inhaling too much chlorine is not to be afraid of it and if a whiff of it gets into the nose not to stop breathing abruptly. If you do, and if you cannot get out of the room before you have to breathe again, you are bound to take a deep breath which will carry the chlorine to all the tender parts of your lungs and a violent coughing spell will be the result. If, on the other hand, you continue to breathe lightly, without taking a deep breath, you can stand a pretty strong chlorine atmosphere for minutes at a time, without any muzzle, safety helmet or other protection. Be careful, however, not to inhale the white fumes which are formed by ammonia and chlorine, in the course of trying to locate chlorine leaks with a rag soaked with ammonia. The coughing spells and the effect on the eyes caused by them are very much worse than with chlorine alone, and last longer. Also, wet chlorine such as emanates from a saturated chlorine water seems to have worse effects than the dry, although only slightly more so.

We have in our plant an oxygen safety helmet, but except for purposes of keeping our men trained in its operation I have never seen it in actual use.

Another purpose for which undoubtedly quantities of liquid chlorine have been shipped abroad from this country is for the manufacture of picric acid, which, in this instance, can be made by first producing chlorbenzol, nitrating it, and then replacing the chlorine by hydroxyl, by treatment with alkali. These are the two only purposes for which, as far as I know, liquid chlorine has been used for war purposes. However, as you see, they are rather limited in their effects and, therefore, hardly deserving of the prominent place accorded them in the newspapers.

In general, I may say and I hope I have been able to demonstrate it in this paper, that liquid chlorine is much more important for peaceful than for war purposes, and we are taking considerable

pride in the fact that in the past few years we have been able, instead of causing destruction of human lives, to save them from the ravages of typhoid fever, and in this way to prove that instead of being an enemy, liquid chlorine is becoming more and more a help and a boon to mankind.

DISCUSSION.

PRESIDENT ADDICKS: Mr. Ornstein speaks in the last part of his paper about the tolerance of chlorine fumes, and says that he does not believe that chlorine, at least by itself, can be used to any great extent in the European battlefields, because you can breathe it with impunity. I am rather inclined to think he has been dealing with men who have acquired a tolerance to noxious gases which is not possessed by the ordinary mortal who meets it for the first time, and that is a very different matter. I do not know anything about chlorine, but I have had a good deal of experience with sulphur dioxide, and in the copper smelters it has been somewhat of a joke to take visitors up to the feed floor of the blast furnace and watch them almost expire, while the men around the smelter rarely notice it. I think that has something to do with the observations in this paper.

G. ORNSTEIN (*Communicated*): Mr. Addicks is perfectly correct when he says that people can acquire tolerance to noxious gases which is not possessed by the ordinary mortal, but this, to my mind, can refer only to breathing a gas with or without immediate inconvenience. I do not doubt that people who inhale a little chlorine for the first time will suffer more inconvenience than others who are to a certain extent accustomed to it, just as we "Chlorine eaters" would feel rather uncomfortable in an atmosphere containing sulphur dioxide, sulphuric acid fumes or other pleasant ingredients of the atmosphere encountered in chemical works.

The point which I intend to bring out, however, is that even though at the time of the accident the body might seem to be very

detrimentally influenced by the inhaling of a strong dose of chlorine, yet there will be *no lasting* effect of any sort, even if this occurs repeatedly and frequently.

My past experience, here as well as in Germany, which extends over quite a number of years, proves this quite conclusively, and I have never heard from any fellow chemist in the same line of business anything which would contradict this conviction.

A paper read before the New York Section of the American Electrochemical Society, in Joint Session with the New York Sections of the American Chemical Society and the Society of Chemical Industry, on February 11, 1916. Called up for Discussion at the Twenty-ninth General Meeting of the Society, in Washington, D. C., April 27-29, 1916.

HYDROGEN FOR MILITARY PURPOSES.

By Edward D. Ardery.*

One thousand cubic feet of hydrogen will lift about 70 pounds; the same volume of coal gas about 35 pounds. According to the purity of the hydrogen, its lifting capacity varies. One process gives gas with a lifting power of about 1.19 kilograms per cubic meter, another 1.183 kg., another from 1.175 to 1.195 kg.

The ascensional force of gases depends upon their specific gravity, temperature, and the barometric pressure of the atmosphere. The ascensional force of any gas equals the weight of air minus the weight of an equal volume of the gas. Hydrogen has twice the ascensional force of pure coal gas, and is universally used for military balloons. Hydrogen permits the employment of smaller balloons, which facilitates transportation and rapid filling, besides affording a smaller target at which the enemy may shoot.

About ten years ago there was constructed a welding torch using oxygen and hydrogen gases, by means of which iron, steel, and other metals could be perfectly welded. About six years ago the blowpipe process of cutting metals was discovered. The construction of oxy-hydrogen blowpipes requires the hydrogen outlets to be capable of supplying four volumes to one of oxygen, for the preheating flames. A torch constructed on this principle cuts almost as well as the oxy-acetylene flame, but is not so efficient in starting the operation of cutting, for the reason that it is necessary, on a flat surface, to make some small projection which the oxy-hydrogen flame can seize, in order to start the heating of the plate. The water vapor produced causes considerable oxidation of the metal when it is brought to the melting point. By using four volumes of hydrogen to one of oxygen this defect is in a

* Captain, Corps of Engineers, United States Army.

measure overcome; but oxy-hydrogen can never be as efficient for welding as oxy-acetylene, for the reason that by the use of excess hydrogen the oxidation by water vapor is only abated and not eliminated. No matter how great the excess hydrogen, the effects of the water vapor still exist. In cutting metals, however, the defects arising in welding are not so marked; and the oxy-hydrogen flame can be used with success where the supply of hydrogen is abundant and inexpensive, as is the case where an electrolytic oxygen plant is used. One cubic foot of hydrogen produces 350 B. T. U., and the temperature produced at the tip of the torch, at four volumes to one, is approximately 4,200° F. (2,315° C.) as compared with 6,300° F. (3,482° C.) produced by oxy-acetylene. Hydrogen for welding is probably best suited only for thin sheet iron, and is perhaps no more efficient than illuminating gas.

Both of these processes might on occasion prove of considerable value in military operations. The welding might be utilized in making light repairs to machinery, gun carriages, wagons, etc. The cutting would no doubt prove useful in cutting débris and wreckage, destroying wire entanglements, cutting bridge members, railroad track, etc.

For military purposes, however, hydrogen would find its greatest use in inflating balloons, either captive or free. To generate the hydrogen gas readily and in sufficient quantities, recourse has been had to various processes. Probably the first method used consisted in employing iron filings and dilute sulphuric acid. In this process the iron filings should be free from rust, and the gas evolved should be cleaned by passing through a water seal and lime purifier. The reaction is given by the formula:

$$Fe + H_2SO_4 = FeSO_4 + H_2$$

Similarly, zinc may be used instead of iron. The gas from zinc and sulphuric acid is purer than when iron is used. 100 lb. of sulphuric acid and about 140 lb. of zinc give 1,000 cubic feet of hydrogen. A balloon with a capacity of 16,000 cu. ft. would thus require about two tons of these materials.

In the Russo-Japanese war the Russians used a process based on the action of aluminum on sodium hydroxide. This method presupposes an ample water supply, and has the drawback that it requires 5½ kg. of materials for every cubic meter of hydrogen

produced. The apparatus consisted of sheet metal containers, each of which was partly filled with sodium hydroxide. The aluminum chips were held in a gauze drum, a portion of which rested in the liquid. From the producer, the gas passed through the washer and from there to the balloon.

In the Morocco campaign, the Spanish government used a producer developed by Schuckert & Co. Instead of using aluminum, silicon was employed. At temperatures of from 80° to 90° C. the action of this element on sodium hydroxide is energetic. The temperature need not be attained by the use of fuel if the natural development of heat during the solution of the caustic soda in water, while forming the solution, is utilized. Preparations for starting the generator consist merely in pulverized caustic soda being poured during stirring into a vessel containing water, thus getting a solution of 90° C. in temperature. By turning on a cock this solution is admitted to the generator vessel, and silicon is added. During the formation of the gas, which lasts about 50 minutes, water is again run into the dissolving vessel, and caustic soda in pieces added, which quickly dissolves with the aid of the hot hydrogen touching the sides of the solution vessel. This enables a new cycle to be commenced with only a few minutes interruption, at the end of every generating process. When the formation of gas is finished, the generator contains a solution of water-glass, a non-injurious liquid, which can be let out without special precaution. The temperature reached does not exceed 110° C. The apparatus is made of iron, and not being subject to chemical or mechanical destruction, it is of practically unlimited durability.

The French have used ferro-silicon instead of silicon. The producing apparatus is called "Silicol." Another method originated by the French is called the "Hydrogenit" process. This is particularly adapted for use where an abundance of water is not available. "Hydrogenit" is a mixture of finely powdered ferro-silicon and sodium-calcium oxide. It is a gray, sandy substance, which, even in a closed receptacle, burns with a large production of hydrogen. The mixture is ignited by means of a match or a small amount of ignition powder. It comes in sheet metal containers, and is said to keep indefinitely at normal temperatures. These containers are placed bodily in the producer and fired. The

producer is surrounded by a water jacket, the contents of which are eventually converted into steam. Towards the end of the process, the steam is shot into the chamber to accelerate the action. The gas is washed in water and then dried by passing through screens of sawdust and coke.

Calcium hydride, a substance known commercially as "Hydrolith" (CaH_2), if dropped into water, evolves hydrogen rapidly.

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$$

The objection to it is its excessive cost. A sodium base may be used instead of calcium, but great care is necessary to prevent ignition of the hydrogen by the heat of the chemical reaction. "Hydrone" is another substance that requires only the addition of water to produce hydrogen.

A German corporation has perfected the old method of producing hydrogen by passing steam over red-hot iron filings. The steam is dissociated, the oxygen combining with the hot iron to form black oxide of iron (Fe_3O_4), leaving hydrogen free. The iron is then regenerated by blowing over the oxide hot water-gas containing a large percentage of carbon monoxide. The black oxide gives up oxygen and is reduced to spongy iron. The process may be made continuous by using two ovens.

In manufacturing nitrogen and oxygen from the air, low temperatures are employed, but these temperatures are not low enough to effect the separation of hydrogen from water gas. Water gas consists of about 50 percent of hydrogen, carbon monoxide, and some nitrogen. It also contains a comparatively small percentage of CO_2, which is first eliminated by passing the gas over caustic potash. The gas thus purified is compressed to about 30 atmospheres, and cooled to a temperature in the neighborhood of the boiling point of oxygen, say 200° C. The liquefiable constituents are the CO and N, whose critical temperatures are, respectively, –136° and –146° C. When allowed to escape from an open valve at the temperature of its surroundings, hydrogen, however, does not cool, but rises in temperature. Thus the regenerative method applied in the liquefaction of air is not applicable for cooling down water gas. Liquid air is therefore resorted to, the requisite degree of cold being obtained by allowing it to evaporate. In spite of the efforts to eliminate CO_2 and water vapor, traces of these

bodies pass into the separating apparatus and are deposited there in solid form, ultimately obstructing it after the lapse of a certain time. By having duplicate plants, one can be worked while the other is brought back into working shape by heating it and blowing gas through it.

The Signal Corps of the U. S. Army has made experiments with a view to obtaining hydrogen by refrigerating illuminating gas.

A method invented by two Dutch engineers is used both in Germany and in Russia. This process uses the gas produced by the fractional distillation of crude oil and tar. The gas is passed through a layer of hot coke, whereby the hydrocarbons break up with ultimate liberation of hydrogen. The product delivered contains from 2 to 3 percent of CO, which is removed by subsequently treating with hot sodium oxide. Oil-gas, crude oil, petroleum by-products, tar, benzol, or benzine may be employed in the same process. Charcoal can be used instead of coke. The oil, which has been previously heated, is introduced as a spray at the top of the producer. The coke is brought to a white heat by a hot-air blast. As the oil eventually cools the coke, production is intermittent.

Hydrogen is also a by-product in the electrochemical manufacture of caustic soda and sodium from sodium chloride.

Hydrogen may be obtained from the electrolysis of water by using lead electrodes and a dilute sulphuric acid electrolyte, or iron electrodes and a 10 to 20 percent solution of potash. If a solution of KOH is used, electrolysis causes the oxygen to combine with the anode, while hydrogen is liberated at the cathode. At intervals the decomposed water has to be renewed, while the potash remains in solution, and there is practically no loss. The electromotive force required is about 3 volts per cell.

Our army installed a plant at Fort Omaha, Nebraska, for generating hydrogen by the electrolysis of water. Thirty cells were used. 1500 amperes of direct current were passed through the cells in series. The voltage varied from 85 to 120, depending on the internal resistance of the cells.

In the original electrolytic plants each cell formed an independent unit, and had with the others a positive and a negative connection, and, furthermore, a separate pipe line for hydrogen

and for oxygen. The filter press system of Sürth came into use about eight years ago. The Sürth system is used extensively by Germany for military purposes. The apparatus consists of a number of cells forming at once the electrodes and the storage tank for the electrolyte. The cells are composed of a special metal which is attacked by neither the oxygen, alkali, nor electric current. These cells are pressed together and form a hermetically closed tank. The electrodes are connected in series. The separation of the gases formed is effected by means of special asbestos tissue. This tissue is placed between the anode and cathode, and separates them positively from each other. At the same time, it permits an easy passage for the electrolyte, and insulates both electrodes from each other. In this manner they form a bipolar electrode; that is, they are positive at one side and negative at the other. Each electrode has in its upper part two connecting canals. One of them has the connection to the positive side and the other has a connection to the negative side, so that all oxygen goes in one canal and all hydrogen in the other. The whole apparatus is filled with electrolytic solution. In the interior of the apparatus there is no accumulation of gas. The electric current goes through the whole apparatus and develops on the surface of each electrode the corresponding gas. For an apparatus of 180 to 200 cells there is provided only one draw-off for hydrogen and one for oxygen. There is only one intake for water. Electrodes that have been working four years have shown no sign of wear.

Hydrogen gas from oil-gas is about 98.4 percent pure, with a specific gravity (air = 1) of 0.087 to 0.092. From water gas the hydrogen is 97 to 97½ percent pure; but if this be passed over soda-lime the resulting gas contains as its only impurity 0.6 to 0.8 percent of nitrogen. A percentage of 97 to 97½ hydrogen corresponds to a density of 0.094, while when the percentage of hydrogen is raised to 99.2 or 99.4, the density falls to 0.077. Schuckert's metallic silicon process gives hydrogen at least 99 percent pure, and free of poisonous or injurious admixtures. The Sürth electrolytic process gives gas 99.8 percent pure.

Stationary plants, usually providing for generation on a large scale, must necessarily be designed along lines more economical than for portable plants. Stationary plants would find use at

aeronautic establishments, army centers, and at points where gas is generated to be compressed into cylinders for shipment. Stationary plants may have capacities for generating 300 cubic meters and upwards per hour. The smaller sizes of apparatus would probably weigh about 4000 kg. net, or 5500 kg. packed for ocean shipment; the larger sizes, 9500 kg. net, and 12,000 kg. gross, no piece weighing over 2000 kg. The electrolytic plant installed at Fort Omaha in 1908 had a capacity of 3000 cu. ft. (85 cu. m.) per hour. To follow an army's movements, portable plants are necessary. These should permit of being mounted on cars or wagons. Some plants can be set up on shipboard, some on three or fewer railroad cars, and others on wagons. The capacity of portable plants varies from 9 cu. ft. (0.25 cu. m.) per hour to (56,500 cu. ft.) 1600 cubic meters per hour.

The weights of portable plants depend, of course, on the capacity and type of plant. Schuckert's generator cars weigh about 2000 kg. each, and the scrubber cars about 1700 to 2100 kg.

In comparing the relative cost of portable plants and stationary plants distributing by means of steel tubes, consideration should be given to the cost of the tubes, their weight to be transported, and the cost of compressing the gas.

For transporting in campaign, hydrogen may be absorbed by some chemical substance dissolving it or giving with it a combination capable of restoring it easily and rapidly whenever wished. Hydrolith and hydrone are in this class. Or, the gas may be compressed in steel tubes. Some French tubes are about 4 meters long, 270 millimeters interior diameter, and 9 mm. thick. Other dimensions are used at sea and in the colonies. In order to avoid explosions, tubes have been tried with diameters of 45 to 400 mm.

Our service employs cylinders about 7 feet (2 m.) long, and 5½ inches (14 cm.) in diameter; and also some about 4 feet (1.2 m.) long and 8½ inches (22 cm.) in diameter. They are made of cold drawn seamless steel tubing.

The weight of steel cylinders is less than the weight of the iron and sulphuric acid necessary to produce an equal volume of hydrogen. The weight of our tubes does not exceed 100 lb. (45 kg.) each. In the French service, each wagon carrying tubes weighs 3000 kg. for about every 15 kg. of gas transported, or about 200 times the weight of the hydrogen. They contain 200

liters of gas at 133 kg. pressure; equivalent to about 25 cu. m. at atmospheric pressure. The German flasks hold about 36 liters of gas at a pressure of 130 atmospheres, which corresponds to about 5 cu. m. of balloon space. Some American flasks contain 100 and 200 cu. ft. (3 to 6 cu. m.) In some cases compression is done at from 150 to 200 atmospheres (2200 to 2940 lb. per sq. in.). Pressures as low as 700 lb. (47 at.) have been used, to prevent explosion. Tanks used in welding or cutting are charged to about 100 or 150 lb. (7 to 10 at.) In our service the tubes are tested with hydraulic pressure up to about 5000 lb. (340 at.) and are charged to about ½ of the pressure used in testing. All our cylinders have a safety outlet blowing at 3500 lb. (238 at.) Our 7 feet by 5½ inches (2 m. by 14 cm.) tubes have a capacity of about one cubic foot (28 liters) and are ordinarily charged to 120 atmospheres.

For German conditions it has apparently been found that the best method of bringing gas to the balloons is not to bring the producer to the front, but to send forward the hydrogen in steel flasks. The flasks are transported in caissons, 20 to each vehicle, and it is so arranged that six caissons can be coupled together when the balloon is to be filled. The French have some wagons that carry six tubes. The transportation of hydrogen in steel tubes is quite an old practice. The English have used tubes since 1882; the Italians, since 1887.

The Germans fill a 600 cubic meter balloon from 120 flasks in about 20 minutes. Using oil gas for producing hydrogen requires one to two hours to fire up. According to the size of the plant being used, Schuckert's metallic silicon process allows of a full production of hydrogen to be reached in from 10 to 45 minutes from the time the command is given. Other processes require different periods of time before gas becomes available for inflation; so the compressed gas in flasks has a considerable advantage as far as the time factor is concerned. Their two principal objections are the danger of explosion and the dead weight to be carried.

A pipe line for carrying hydrogen is in successful operation in Germany. The line is 4½ kilometers long, and can supply 1000 cubic meters of gas daily. This requires a pressure of 1000 millimeters (water column.) It discharges into a storage tank. The joints of the pipe are welded autogeneously for most of the length, unions being installed at long intervals.

The cost of production varies, of course, with the size of the plant, market and labor conditions, and the process used. Some of the *alleged* costs per cubic meter (35 cu. ft.) of hydrogen gas, according to the process used, are: Ferro-silicon 20 cents, hydrogenit 32 cents, hydrolith 100 cents, steam and hot iron filings 3 cents, distillation of crude oil and tar 3½ cents, water gas 25 cents, old method of iron and sulphuric acid 25 cents, calcium hydride 175 cents, silicon and caustic soda 210 cents. By electrolysis, 1500 amperes produce 23 cu. ft. (0.66 cu. m.) of hydrogen and 11½ cu. ft. (0.33 cu. m.) of oxygen per cell per hour.

As I have shown above, the lifting power of a balloon depends on the gas used to inflate it and on the volume of the balloon. The temperature and barometric pressure of the atmosphere affect the density of the gas, and hence its ascensional force. A captive spherical balloon cannot be used when the wind is greater than twenty miles an hour.

The usual fixed balloon has a capacity of 600 cubic meters. The dirigible balloons have capacities up to possibly 60,000 cubic meters. It is stated that the German dirigible that descended in France in 1913 had a volume of 20,000 cubic meters and a lifting capacity of 20 tons. The normal working internal pressure is understood to be 2 oz. per square inch (0.0085 atmosphere.) Cotton, silk, goldbeater's skin, and various rubberized fabrics have been used as balloon envelopes. Silk is objectionable on account of its cost, and on account of its accumulating static electrical charges. Great Britain has used goldbeater's skin. Rubberized fabrics oxidize and crack. The envelope should be strong, elastic, impermeable to gas, water repellant, and of light weight. Chlorine attacks balloon envelopes.

Hydrogen is so light that in case of leaks, even low down in the envelope, the gas rises; but if mixed with air in a balloonet it becomes heavier, descends, and may be exploded by a spark from the engine.

Without going into the theory of ballooning, I might add that unless the balloon envelope is elastic, a rise in altitude of 125 feet (38 m.), or a rise in temperature of the gas of 2½° F. (1.4° C.) necessitates the loss of gas. Goldbeater's skin allows a rise to 2000 feet without loss of gas. As fuel is used up or explosives dropped, the tendency of the lightened balloon is to rise, thus

probably causing a loss of gas. In dirigibles, it must be borne in mind that ordinarily there is sufficient lifting capacity only when the motors are running. If they stop, the vessel must descend or jettison some ballast.

A trip of about 8½ hours from a base in Germany to the English coast would mean the use of about 1½ tons of fuel. If 1½ tons of explosives are carried, a state of static equilibrium will have been attained by the time the coast is reached.

The hitherto too rapidly fluctuating buoyancy of the airship may now be controlled through the use of the graduated motor exhaust, which is evenly distributed by ducts throughout the entire air-jacket between the outer and inner hulls, and the same system enables the passing of hot and cold currents through the air-jacket at the will of the operator. These alternate hot and cool currents expand or contract the gas, producing rapid ascent or descent. This device has assured a static gas, which maintains the airship for long periods at normal buoyancy.

If the air-jacket contains a charge of nitrogen gas, this not only insulates the hydrogen from atmospheric effects, but acts as a sure preventive of fire risk. Both of these methods have proved easy of accomplishment. The exhaust of the motor has been freely discharged into a balloon containing hydrogen, without setting it afire. Experiments with the nitrogen jacket are said to have demonstrated the complete success of this method, which explains the story about the Germans using non-inflammable gas.

Army Building,
New York City.

DISCUSSION.

President Addicks: Papers of this character are timely, because they present the military point of view, which is hard for the layman to comprehend, as all economic laws are turned upside down and only the law of expediency prevails.

C. G. Fink: I consider Mr. Ardery's paper a most timely one. The Government is after a compact apparatus for generating hydrogen, and this subject is an admirable one for the universities

to tackle, because no individual cares to do so, the subject being too broad. It means a comparison of all present methods of hydrogen generation. Mr. Ardery shows us just what the Government requires, an apparatus which can be set up on a freight car and easily conveyed from place to place. Such a self-contained apparatus is preferable to containers which are apt to leak by the time you get to the place of operation.

O. Hutchins (*Communicated*): Considerable work has been done in the research department of the Carborundum Company on the production of hydrogen from silicon and caustic soda. It has been found possible to work with the following equation:

$$2Si + 2NaOH + 3H_2O = Na_2O.2SiO_2 + 4H_2$$

Silicon metal, used in this reaction, contains 90 percent silicon, 2 percent aluminum, the remainder iron and traces of other impurities. A recovery of hydrogen equal to 90 percent of the theoretical is made without taking undue precautions. Theoretically, to produce 1,000 cu. ft. of hydrogen at 0° C. and 76 cm. pressure would require 49 lb. of silicon and 62.2 lb. NaOH.

The method used to produce this hydrogen has already been described by Mr. Ardery, and the method used by the Carborundum Company is essentially similar. The results were obtained in a commercial generator having a capacity of 50 cu. ft. of hydrogen per hour. The methods employed and the apparatus used are exceedingly simple and the cost of producing hydrogen by this method is almost entirely made up of the cost of the silicon metal and the caustic soda.

Costs under normal conditions.

(per 1,000 cu. ft. of hydrogen).

49 lb. of silicon metal, at $180 per gross ton	$3.94
62 lb. 98% NaOH, at $0.40 per net ton	1.27
Cost of raw materials	$5.21

Costs with caustic soda at $100 per ton.

49 lb. of silicon metal	$3.94
62 lb. NaOH, 98%, at $100 per net ton	3.17
Total costs of raw material	$7.11

It thus appears possible to produce hydrogen by this method at a cost less than 1 cent per cu. ft.

President Addicks: In regard to Mr. Hutchins' remarks, the question of the purity of gas seems to be exceedingly important. In the electrolytic process he claims to get gas 98.9 percent pure, whose lifting power is greater than gas 97 to 98 percent pure from some of the chemical processes, and that would have to be taken into account as well as the cost per cubic foot.

E. D. Ardery: The statement by President Addicks, that "all economic laws are turned upside down and only the law of expediency prevails," is true to the extent that military necessity will countenance an apparent disregard of economy that would not be tolerated from a commercial point of view; but it is not to be inferred from this that considerations of economy are entirely subordinated to expediency.

In addition to our having hydrogen-generating apparatus that can be installed on a freight car, Mr. Fink might well carry his point further, so as to show the necessity of providing units that can be set up on motor trucks or wagons. This equipment would often permit of balloons being operated from an advanced base or station at a distance from a railroad.

In his discussion of Mr. Hutchins' remarks, President Addicks wisely points out that in comparing the cost of generating hydrogen by various processes, account should also be taken of the purity of the resulting gas. The nearer pure we obtain the hydrogen, the greater its ascensional force. This increased ascensional force enables us to carry heavier loads with a given size balloon, or it permits us to employ smaller balloons, thereby facilitating transportation, rapid filling, and use in stronger winds, besides affording to the enemy a smaller target for his rifle and artillery fire.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, held in Washington, D. C., April 27-29, 1916.

COBALT AS AN ELEMENT FOR THERMO-COUPLES.

By O. L. Kowalke.

Cobalt and nickel as elements of thermo-couples have many properties in common, such as ductility, high melting point, fairly strong resistance to oxidation, and high electromotive force. When exposed to hot gases, particularly products of combustion, nickel becomes extremely brittle and breaks easily. Such failures of couples are not only exasperating but are also wasteful of valuable time and energy.

Several years ago in this laboratory a rod of cobalt about three-sixteenths of an inch (0.5 cm.) square was forged from an ingot and made into a thermo-couple with "nichrome" as the other element. This couple has been given hard use in fused electrolytes and hot gases, but no break ever occurred. Such satisfactory performance of cobalt led to this investigation. It was proposed to determine the electromotive forces, and their constancy, of different combinations of metals with cobalt when first calibrated and after being subjected to various heat treatments.

Couples Used.—The combinations of metals with cobalt used in these tests are as follows:

Couple No. 1	Cobalt *vs.*	"Nichrome"
" " 2	" *vs.*	"Advance"
" " 3	" *vs.*	"Constantan"
" " 4	" *vs.*	Iron
" " 2B	" *vs.*	Nickel-iron

The "Nichrome" and "Advance" wires were purchased from the Driver-Harris Wire Co.; the "Constantan" from H. Boker; the iron wire from Taylor Instrument Co.; the cobalt from Dr. H. T. Kalmus, of Queens College, Kingston, Ont. Mr. R. C. Schwartz, of the Taylor Instrument Co., donated the nickel-iron alloy, while Mr. W. H. Bassett, of the American Brass Co., had the cobalt drawn into wire. Grateful acknowledgment is hereby made for these courtesies.

Since "Nichrome," "Advance," "Constantan," and iron are stock wires and are well known, no analyses were made of them. Only the cobalt and the nickel-iron alloy were analyzed. The compositions are as follows:

Cobalt			Nickel-iron		
Ni	= 1.20	percent	Cr	= 9.73	percent
Fe	= 1.35	"	Ni	= 61.15	"
Co	= 97.20	"	Fe	= 24.65	"
C	= 0.23	"	Mn	= 3.50	"
S	= 0.02	"	Si	= 0.72	"

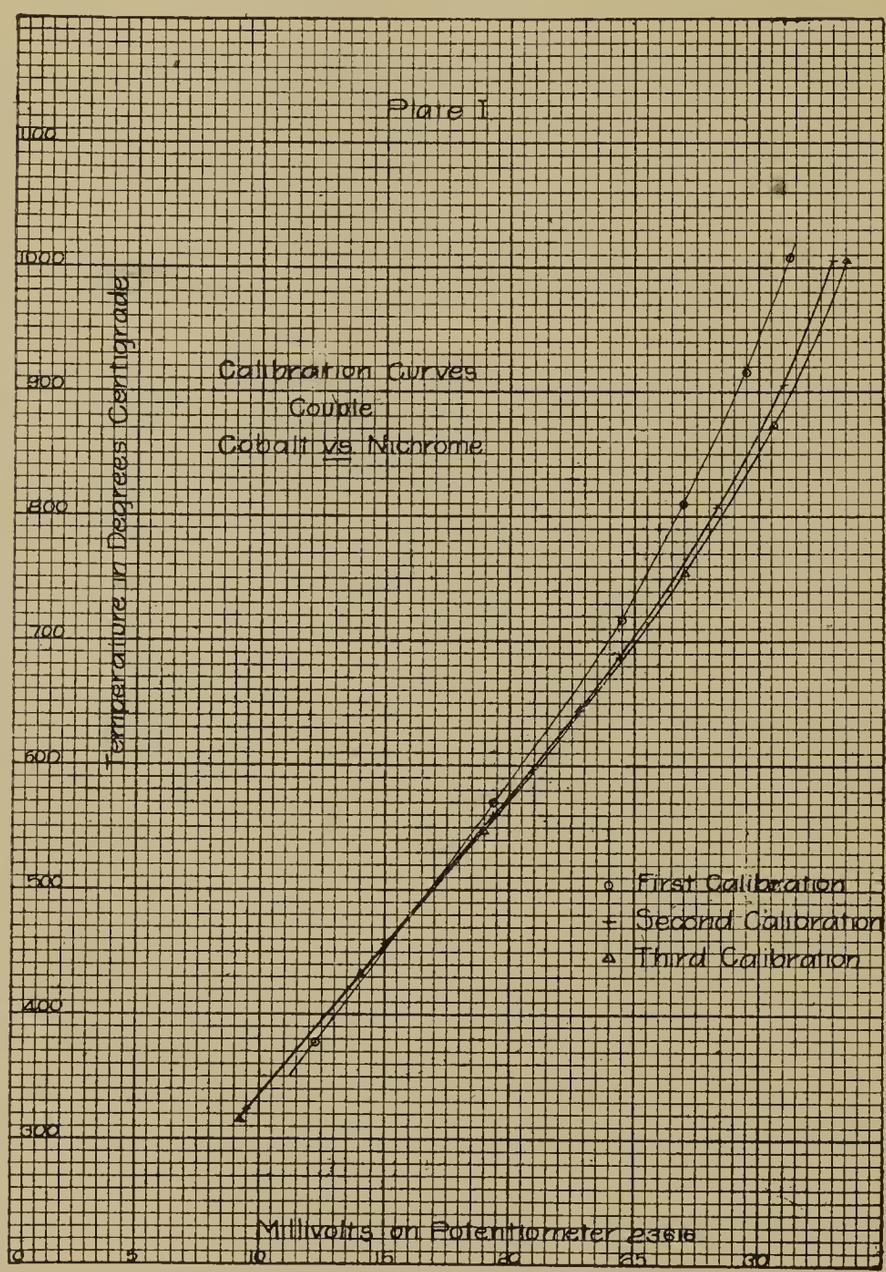

PLATE I. Couple No. 1. Cobalt *vs.* Nichrome.

It was not convenient to obtain these wires all the same size, nor was this necessary, since all measurements were made on potentiometers. The sizes of wires used are given below.

Wire	Gauge B & S	Diameter Inches	Diameter Millimeters
Cobalt	15	0.0599	1.50
Nichrome	10	0.1036	2.60
Advance	15	0.0604	1.51
Constantan	8	0.1271	3.22
Iron	10	0.1025	2.59
Nickel-iron	10	0.1035	2.60

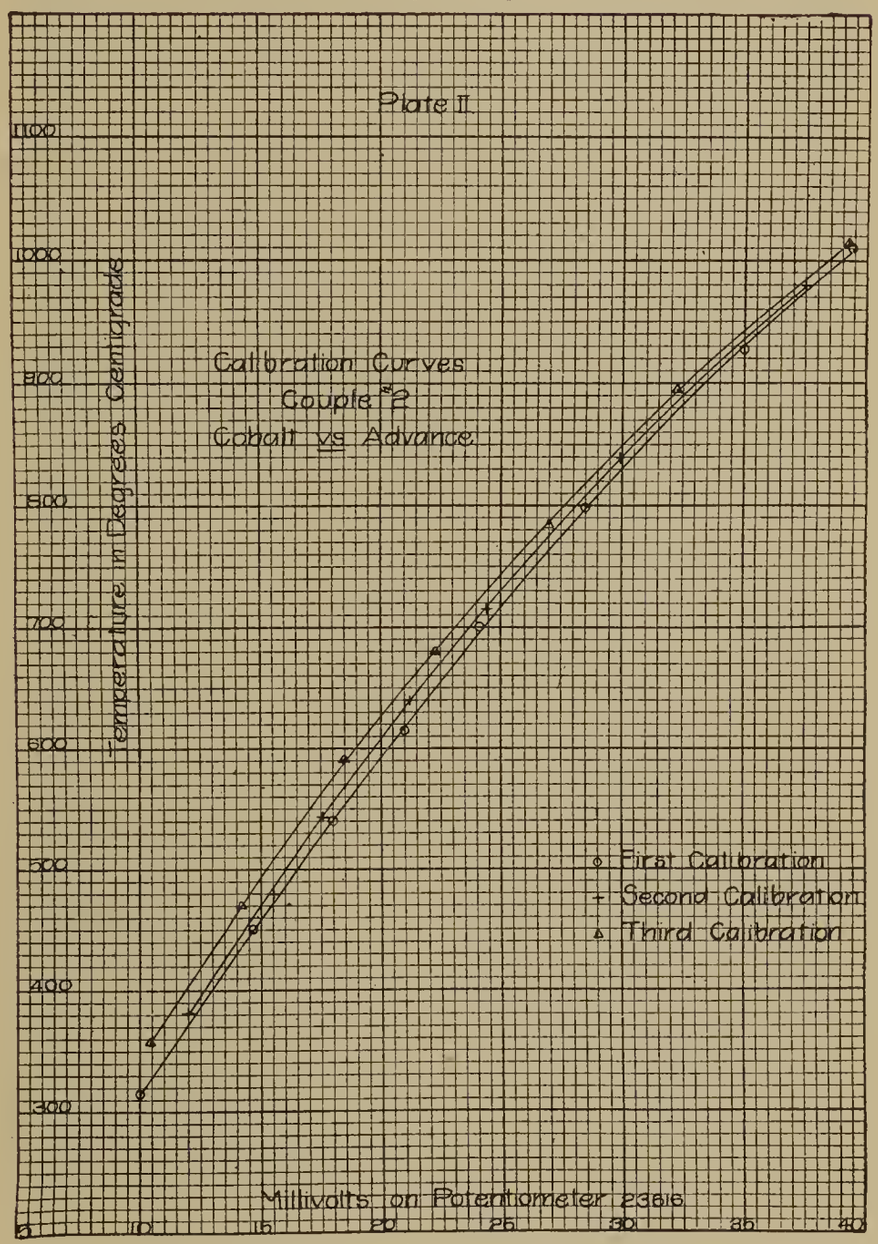

PLATE II. Couple No. 2. Cobalt *vs.* Advance.

The polarity of the couples was not the same, as may be observed from the tabulation below, where "positive terminal" means that terminal attached to the positive binding post of the measuring instrument.

	Positive Terminal	Negative Terminal
Couple No. 1	Nichrome	Cobalt
" " 2	Cobalt	Advance
" " 3	Cobalt	Constantan
" " 4	Iron	Cobalt
" " 2B	Nickel-iron	Cobalt

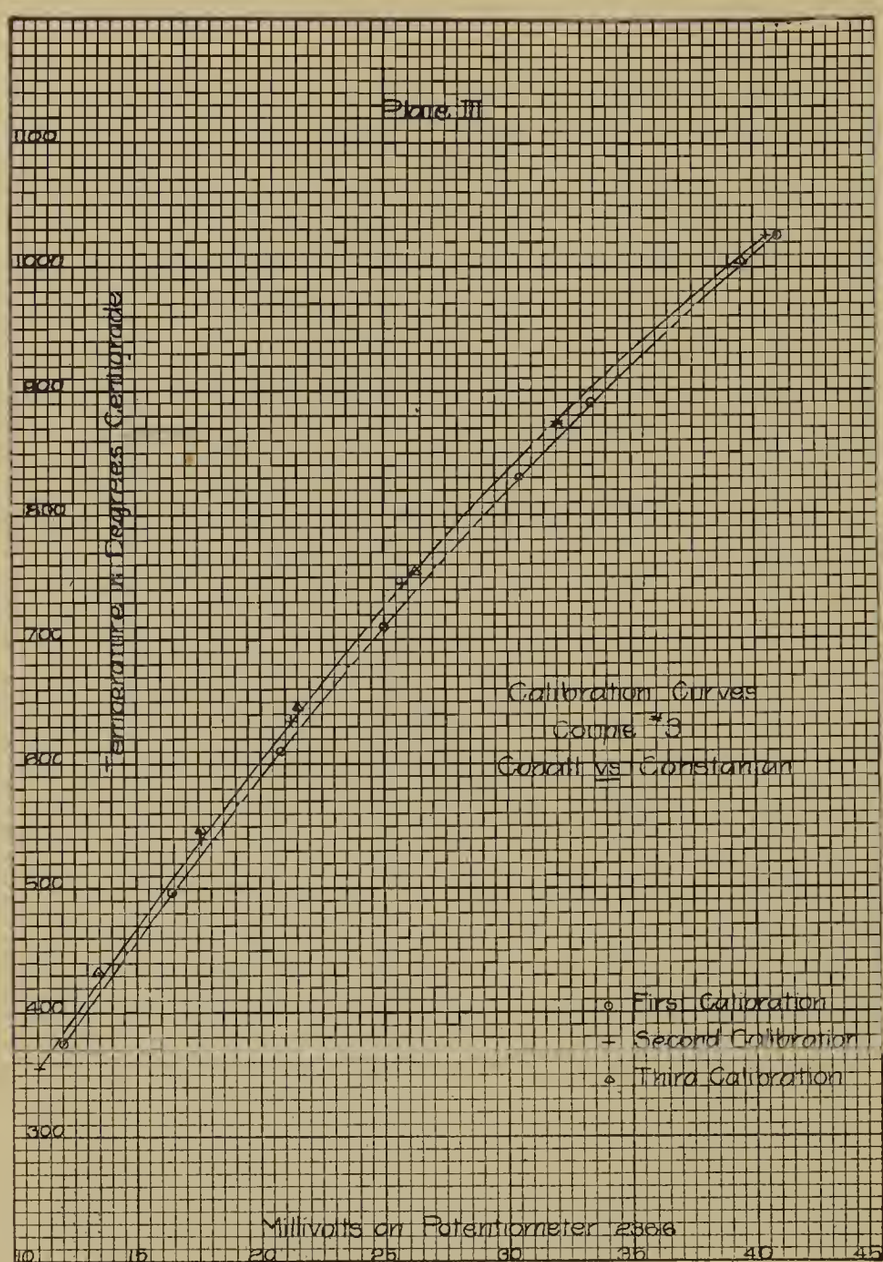

PLATE III. Couple No. 3. Cobalt *vs.* Constantan.

Couples twenty inches long were made from the above wires. To remove any mechanical strains, each was heated for several minutes to a bright red heat by means of the electric current. The wires were insulated from one another by an asbestos sleeve, while lamp cord soldered to the elements served as leads to the measuring instrument.

Equipment Used:—All electromotive force measurements were made on Leeds & Northrup portable potentiometers.

Two platinum *vs.* platinum-10 percent rhodium couples were used as standards. One of these was retained as the primary standard and the other used for making the comparisons against the base metal couples.

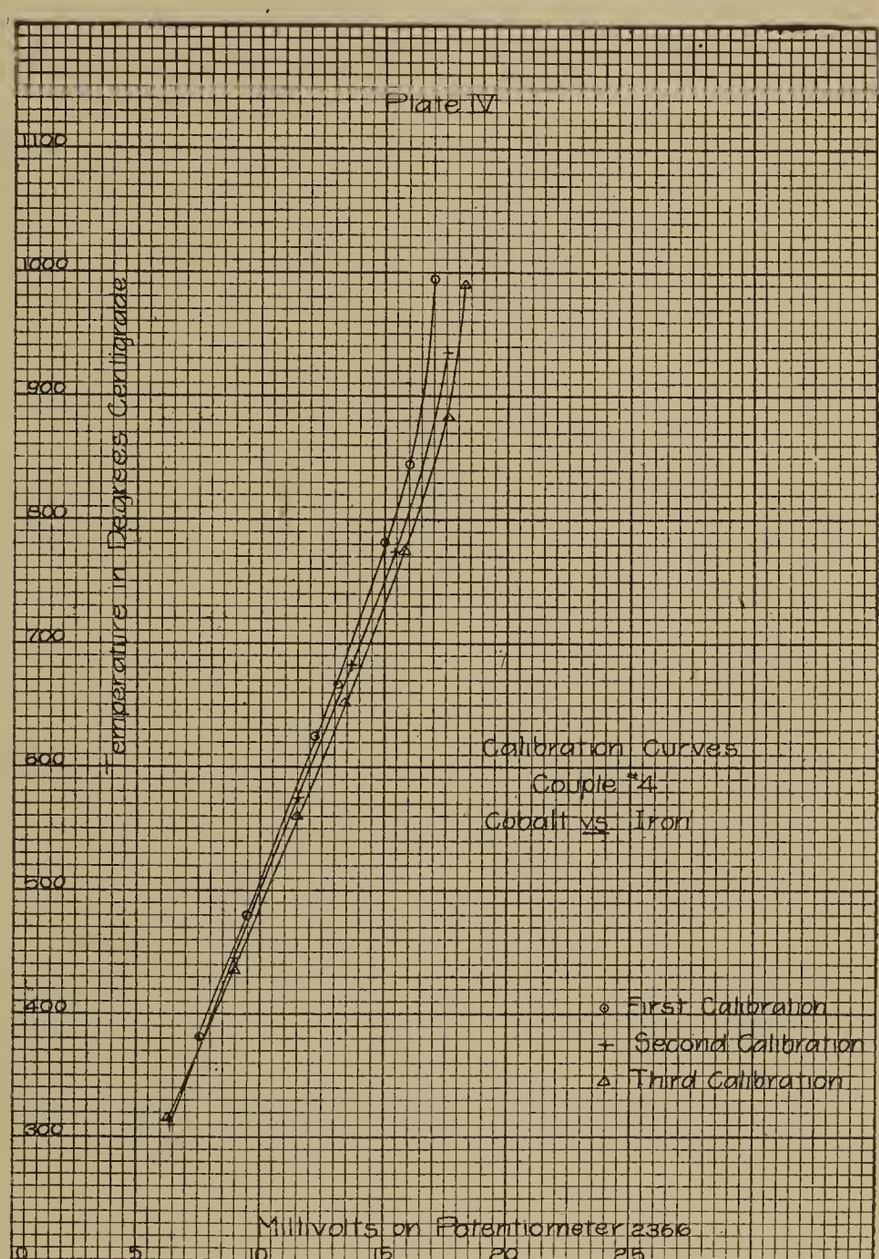

PLATE IV. Couple No. 4. Cobalt *vs.* Iron.

For calibration purposes there was used an electric tube furnace, wound with "Nichrome" ribbon, whose dimensions were 1¼ inches (3.1 cm.) inside diameter by 24 inches (60 cm.) long. A small porcelain tube about 2½ inches (6.2 cm.) long and ½ inch (1.3 cm.) in diameter was supported in the furnace on

rings so that its axis coincided with that of the furnace. The purpose of this tube was to provide a chamber which was heated uniformly and which kept the junctions of the couples the same distance from the walls of the furnace.

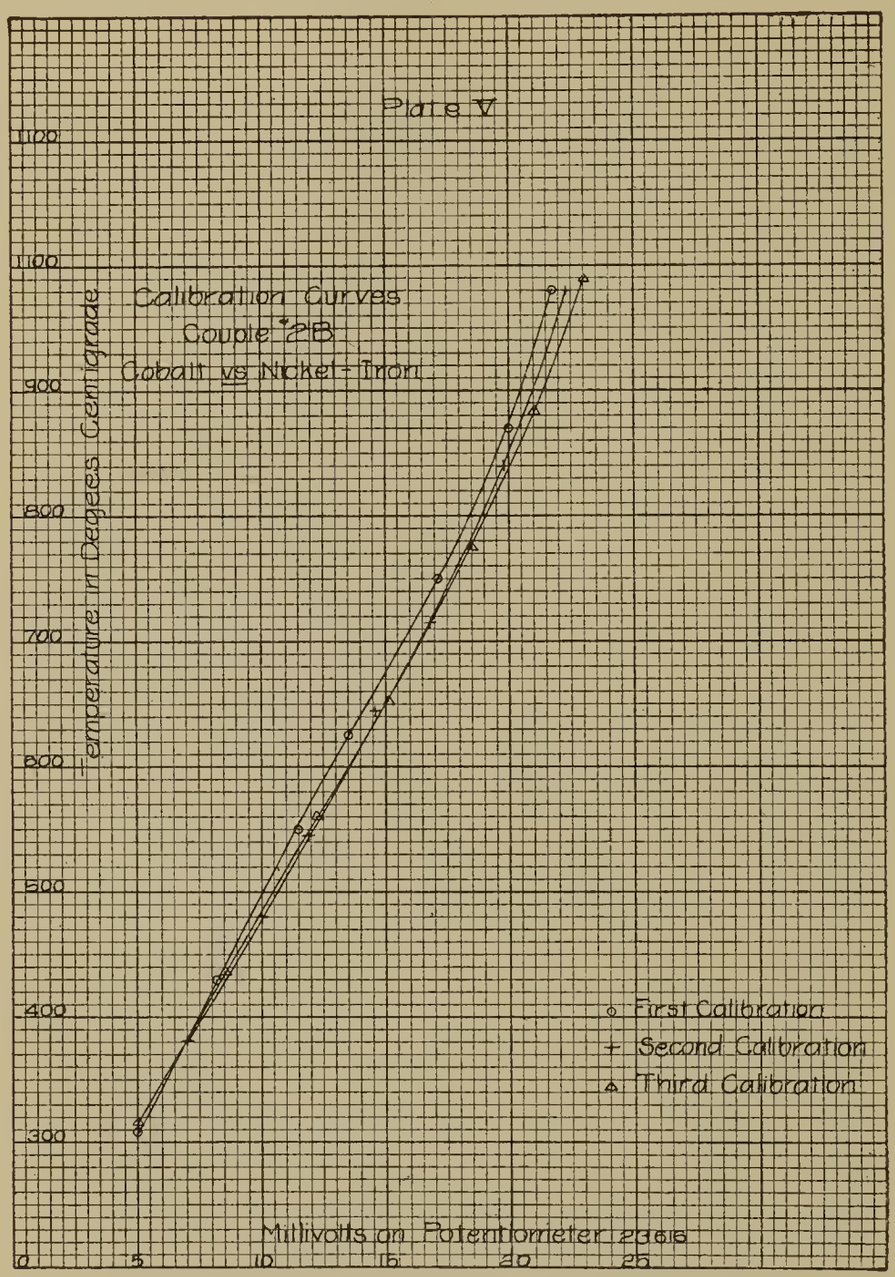

PLATE V. Couple No. 28. Cobalt *vs.* Nickel-Iron.

For heat treatment, an electric furnace having "Nichrome" ribbon wound on a tube three inches (7.5 cm.) in diameter and 30 inches (75 cm.) long, was used.

Procedure:—The platinum couples were first calibrated in the regular manner by observing the electromotive forces at the freezing temperatures of pure zinc and copper, and then calibrated against each other as a check.

In all the calibrations the cold junctions of all couples were kept at 0° Centigrade, and only one base metal couple at a time was compared with the standard platinum couple. All the couples were compared with the standard at intervals of about 100 degrees Centigrade, and at each point the temperature was held constant for a period of at least two minutes to insure the same temperature at the junctions of both couples. The length to which the base metal couples were inserted in the furnace for all calibrations was thirteen inches (33 cm.).

After the various couples were constructed and annealed they were calibrated in the manner described above. Then all couples were tied into a bundle, put into the heat-treating furnace so that the axis of the bundle coincided with the axis of the furnace, and heated for five hours at a temperature varying from 700 deg. C. to 725 deg. C. After this treatment all couples were calibrated separately a second time against the standard. A second heat treatment followed this calibration in exactly the same manner as described above, except that the period of heating extended over 36 hours, during which the temperature varied from 720 deg. C. to 750 deg. C. A third calibration, exactly like the first and second, followed the second heat treatment.

OBSERVATIONS AND CONCLUSIONS.

Conditions of the Wires.—The cobalt element became coated with an oxide film at the first calibration and this coating appeared to increase in thickness with the subsequent heat treatments and calibrations. The wire was malleable and ductile throughout the tests. A larger size of wire will undoubtedly oxidize less and give a longer service.

The "Nichrome" and nickel-iron elements had only a thin oxide coat at the end of the tests.

"Constantan" and "Advance" behaved about alike. A thin oxide film appeared after the first heat treatment, which subsequently became slightly thicker, though not thick enough to cause appreciable deterioration.

The iron element suffered more than any other through oxidation, so that at the conclusion of the tests its size was about one-fourth that at the beginning.

Electromotive Force.—The results of these tests are shown in Plates I to V. It will be apparent from the slopes of the

graphs in Plates I, IV, and V, that the electromotive forces increase at a diminishing rate with an increase in temperature, while in Plates II and III the electromotive forces show an augmented rate of increase with a rise in temperature. For couples 1, 4, and 2B, as shown in Plates I, IV, and V, cobalt is the element attached to the negative terminal of the measuring instrument, which means that the current is flowing from the cobalt to the other element. In couples 2 and 3, as shown in Plates II and III, cobalt is attached to the positive terminal of the measuring instrument, which indicates that cobalt is at a lower potential than its companion element.

Inspection of the five plates makes it apparent that cobalt appears to gain in electrical potential as a result of being heated to high temperatures for extended periods of time. In Plates I, IV, and V, the electromotive force at any given temperature has increased from the first calibration to the third, and for these couples the potential is from cobalt to its companion. In Plates II and III, the electromotive force at any given temperature shows a decrease from the first to the third calibration. In these couples the increase of potential of cobalt serves to diminish the resulting couple potential.

Constancy.—With the exception of Couple No. 3, all couples seem to show a calibration change as the result of heat treatment. The error is not larger than has been found previously.[1] Couple No. 3, composed of cobalt and "Constantan" has shown itself to be the best of this group.

Cobalt should enjoy an important place among thermo-elements. It is robust, it can be obtained fairly pure, it does not appear to get brittle like nickel, and it gives a high electromotive force. The only drawback at present is its high price.

In conclusion, I desire to acknowledge the assistance of Mr. J. B. Edwards, Jr., in obtaining these data.

Chemical Engineering Department,
University of Wisconsin.

[1] Trans. Am. Electrochem. Soc., 24, 377 (1913).

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, held in Washington, D. C., April 27-29, 1916.

THE ELECTRICAL RESISTANCES AND TEMPERATURE COEFFICIENTS OF NICKEL-COPPER-CHROMIUM AND OF NICKEL-COPPER-MANGANESE ALLOYS.[1]

By F. M. Sebast and G. L. Gray.

The object of this investigation was to determine the effect of the addition of chromium and of manganese on the electrical resistivity and temperature coefficient of copper-nickel alloys, with a view to obtaining a new and better resistor alloy than those in use at present.

All resistors may be placed in one of two general classes—those used for the dissipation of energy and those used in instruments and standard resistances.

Resistors of the first class generally have a high resistivity with a moderate temperature coefficient. They should melt only at a high temperature and should not corrode when worked hot. There are a large number of these alloys on the market at the present time. A few of these are given in the following table:

Trade Name.	Constituent Metals.	Resistivity Micr. per cm. cube.	Temp. Coeff. Per Deg. C.
18% German Silver	Cu, Ni, Zn	33	0.00031
Climax	Fe, Ni	87	0.00067
Ferro-Nickel	Fe, Ni	28	0.00210
Krupp	Ni, Steel	85	0.00070
Nichrome	Fe, Ni, Cr	95.5	0.00043

Some of the later Placet alloys have a resistivity as high as 111 microhms per cm. cube, with a temperature coefficient of 0.00016.

The second class of resistors has very low temperature coefficients with moderately high resistivities. They must also have a low thermo-electromotive force against copper. This latter requirement is the one which most of the present resistors in this

[1] The investigations reported in this article were suggested by Dr. M. S. Hunter and were submitted by the authors to the faculty of the Rensselaer Polytechnic Institute in part fulfilment of the requirements for the degree of Electrical Engineer.

class fail to meet. Manganin is the most satisfactory alloy in this respect, having a thermo-electromotive force of only about 3 micro-volts per degree. Constantan, which is very good with respect to resistivity and temperature coefficient, has the high thermo-electromotive force of 40 micro-volts per degree. The following table gives the resistivity and temperature coefficient

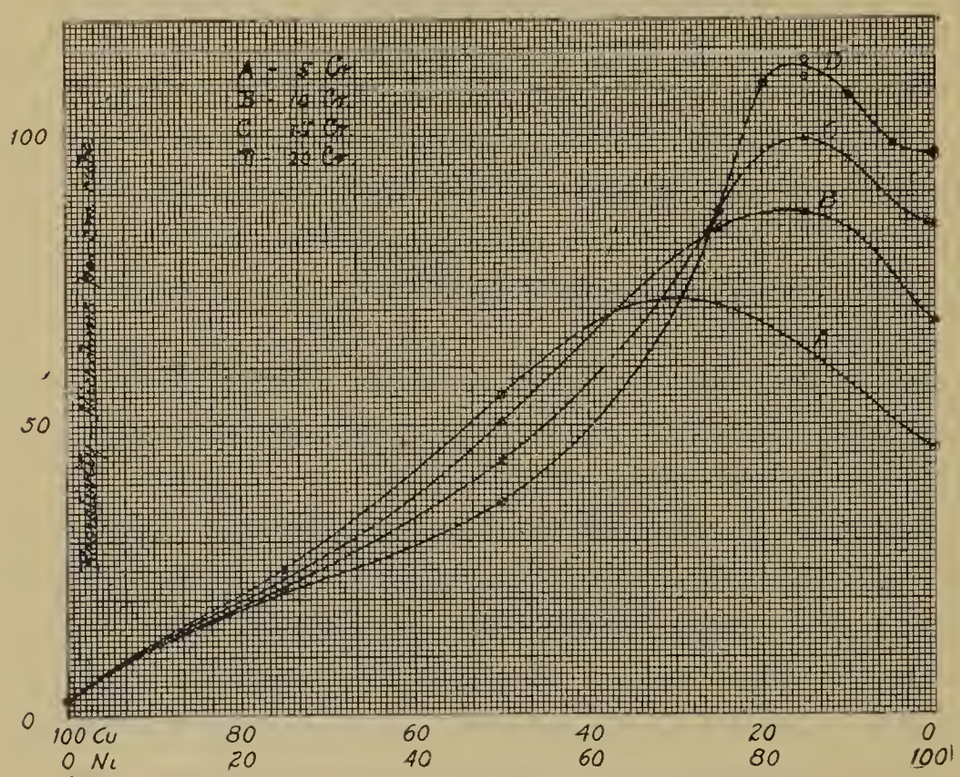

PLATE I. Resistivity of Cu-Ni-Cr Alloys.

of some of the more important alloys now used for making up accurate resistances.

Trade Name.	Constituent Metals.	Resistivity Micr. per cm. cube.	Temp. Coeff. Per Deg. C.
Manganin	Cu, Ni, Mn	42	0.000011
Constantan	Cu, Ni	50	0.000005
Ia Ia	Cu, Ni	47	0.000005
Advance	Cu, Ni	49	0.000018

The resistivity of an alloy has long been known to be intimately connected with its constitution. Ever since the researches of Matthiessen,[2] in 1859-1865, two classes of alloys have been recognized: (1) those in which the resistivity of the alloy is approximately a linear function of the concentration of the component

[2] Report of Submarine Telegraph Committee, Blue Book, London, 1861.

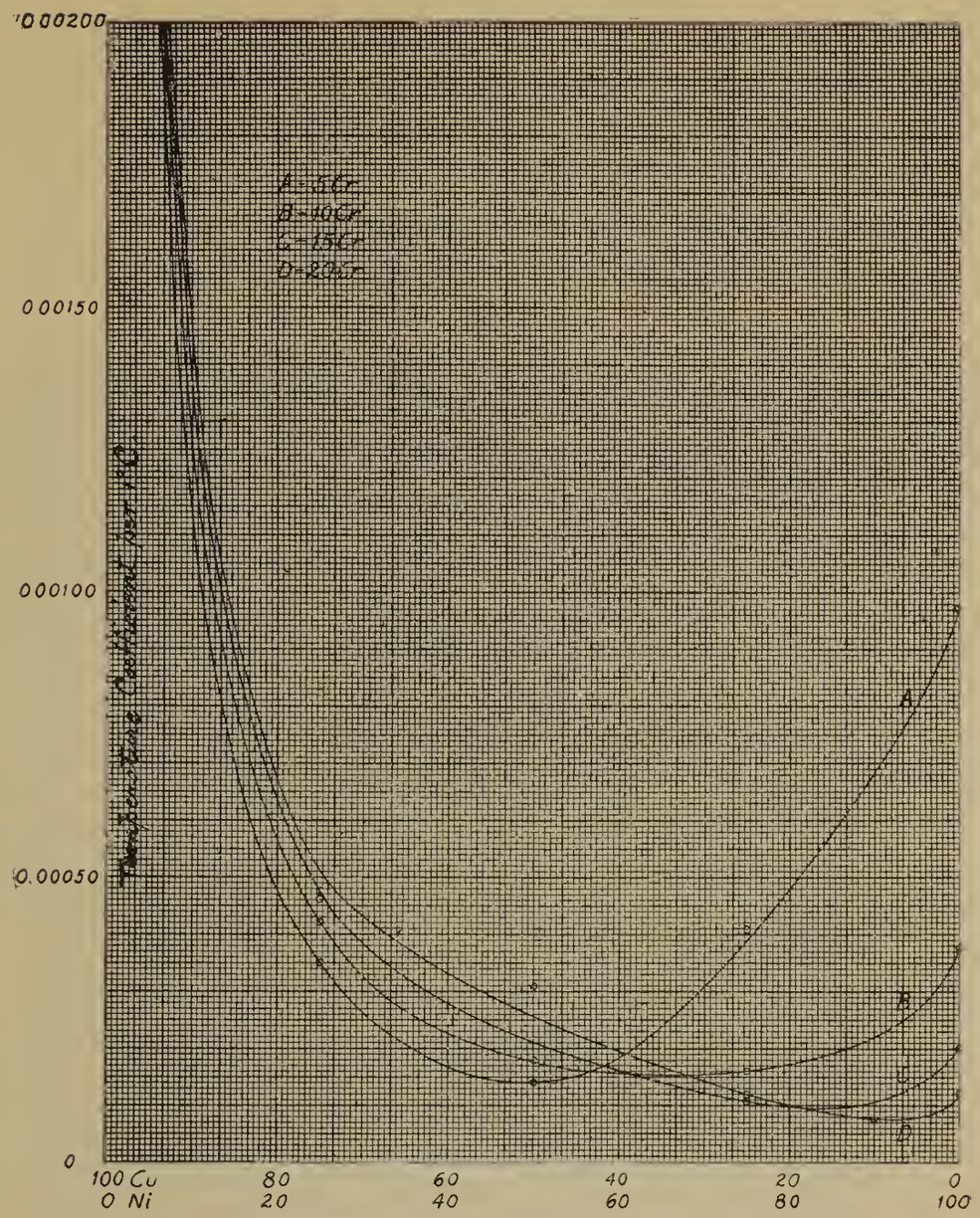

PLATE II. Temperature Coefficient of Cu-Ni-Cr Alloys.

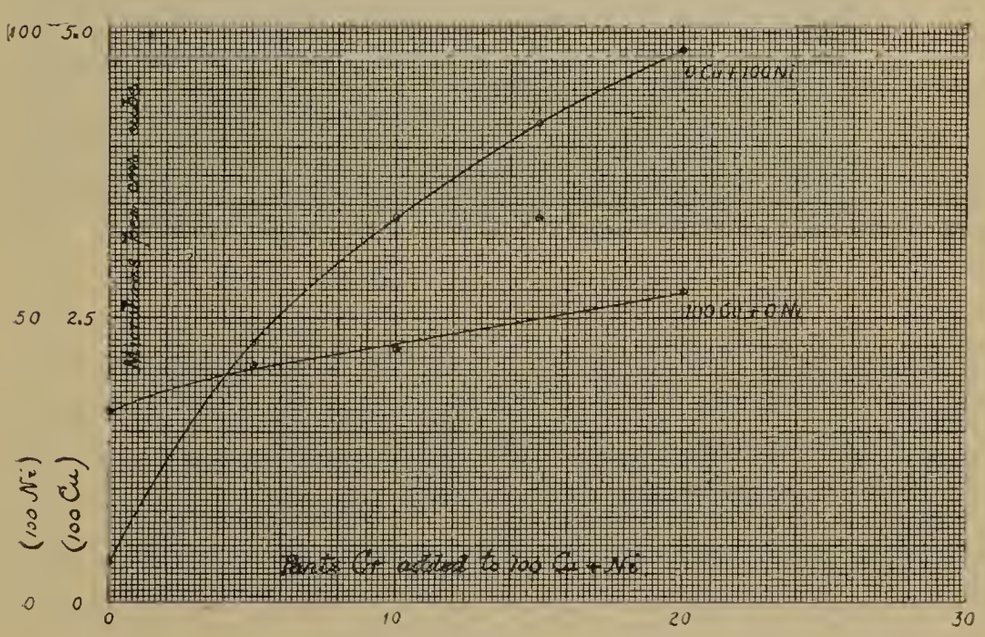

PLATE III. Resistivity of Cu-Cr and of Cu-Ni Alloys.

metals, and (2) those in which the addition of small quantities of one metal to the other produces a marked increase in resistivity. In the case of the first class the resistivity may be calculated by means of the rule of mixtures.

The true relation between the resistivity and the constitution of alloys was first recognized by Le Chatelier. He stated that when

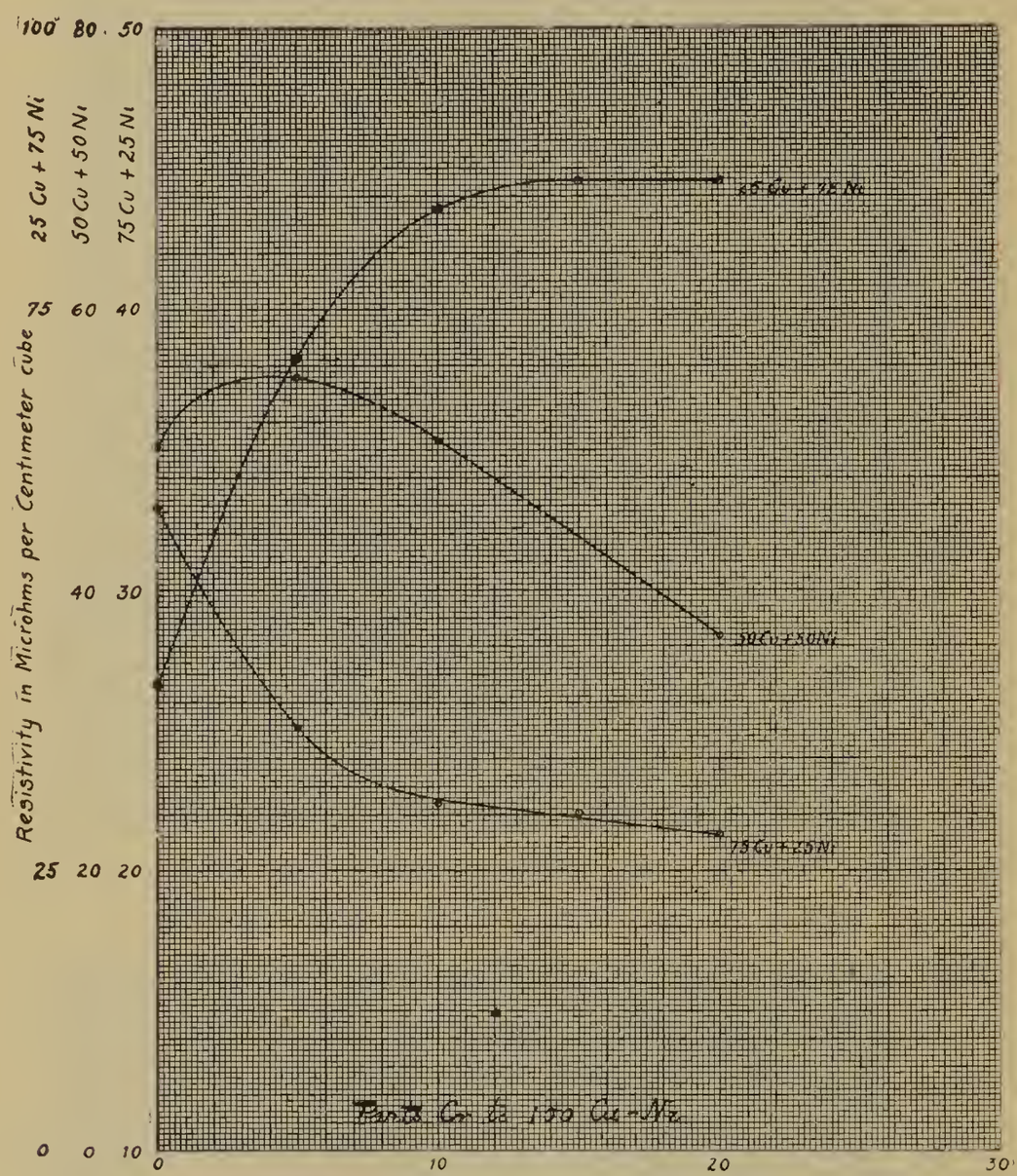

PLATE IV. Resistivity of Cu-Ni-Cr Alloys.

the resistivity varied as a linear function of the concentration the components of the alloy were arranged side by side in the crystalline condition. In this case the component metals combined to form a series of eutectic alloys. The marked increase by small additions, he supposed to be due to mixed crystal formations. In this case one metal was capable of holding the other in solid solution.

These two cases of Le Chatelier represent the two extreme cases: insolubility throughout the whole range and complete solubility throughout the whole range of concentration. Geurtler pointed out a third case; *viz.*, solubility at low concentrations and insolubility at higher concentrations. The form of the curve in this case would naturally be that of a combination of the curves of first two cases.

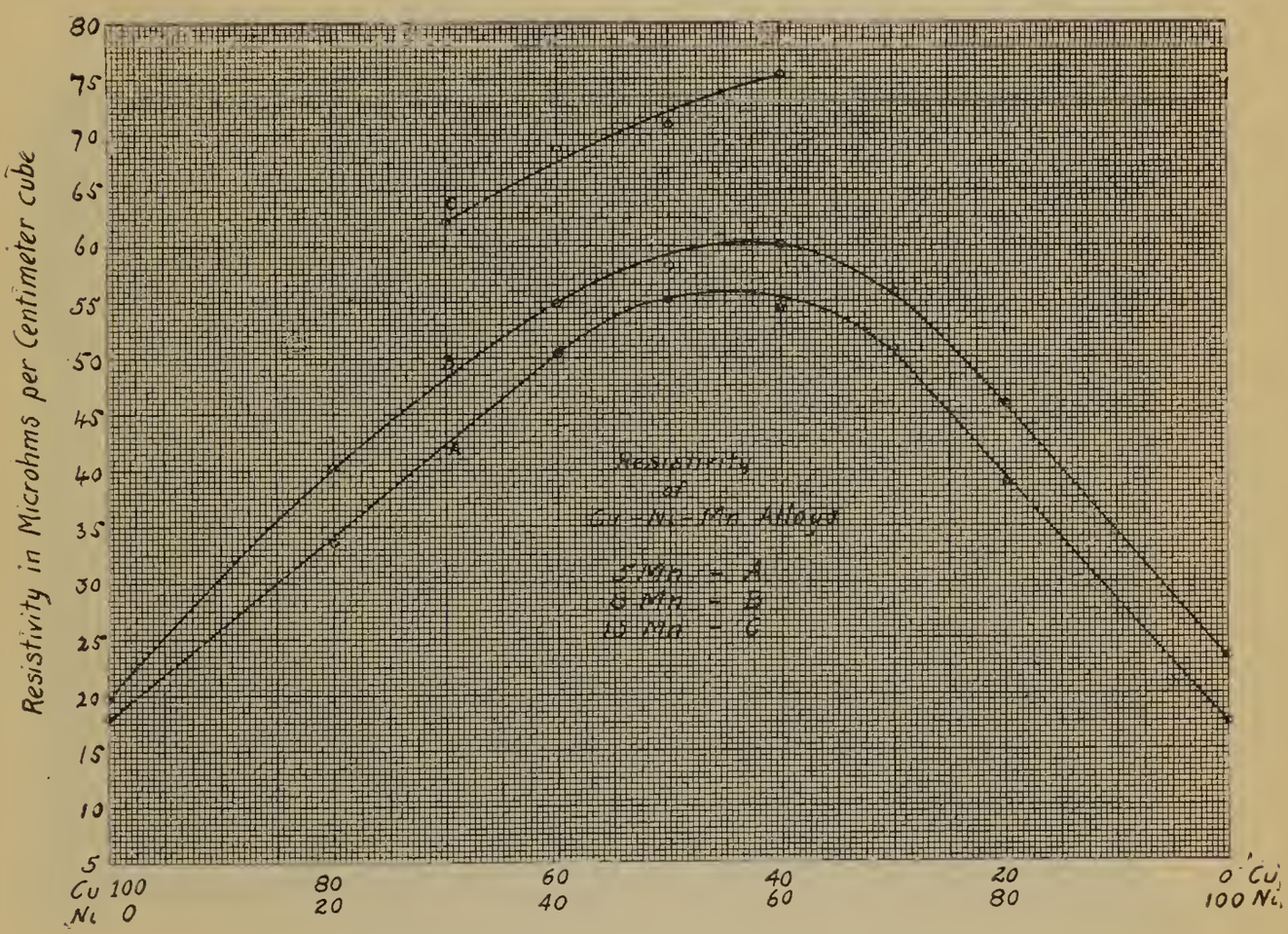

PLATE V. Resistivity of Cu-Ni-Mn Alloys.

Now, it is well known that, in general, all solid conductors undergo a change of resistance with temperature. The change produced is approximately proportional to the change of temperature.

$$\text{Thus } R_t = R_{t_0} [1 + \propto (t - t_0)]$$

where R_t = resistance at temperature t

R_{t_0} = resistance at temperature t_0

$\propto$ = temperature coefficient of resistance

For nearly all pure metals the value of $\propto$ is about 0.0042 per degree Centigrade.

For eutectic alloys it has the same value, while for alloys of the solid solution type it is usually much smaller and may become zero or even negative.

PREPARATION OF SPECIMENS.

The specimens were prepared in the following way: The component metals were weighed out in the desired quantities with an accuracy of 1 percent. The small pieces of metal were then put into an alumina crucible and were melted in an Arsem vacuum

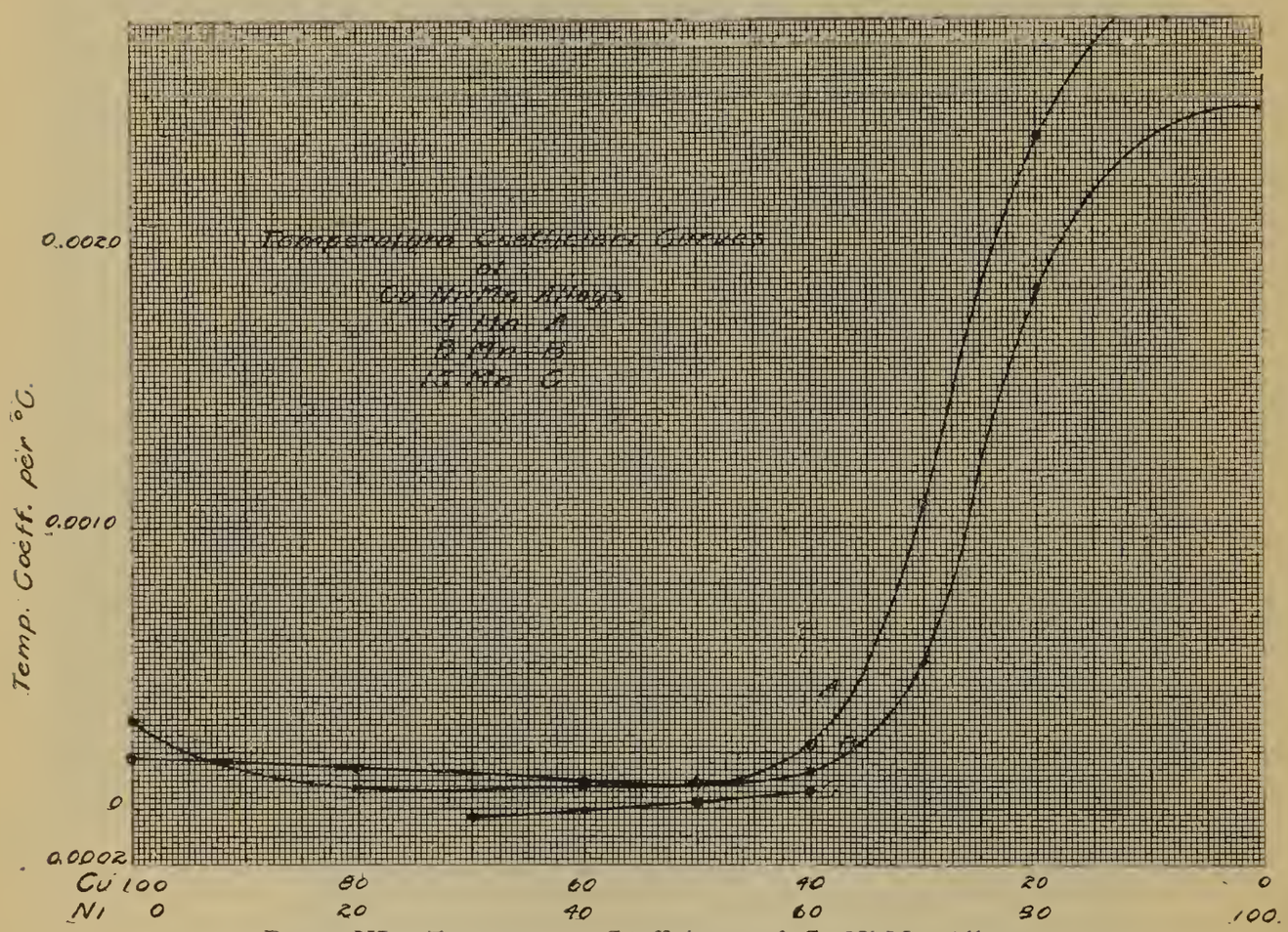

PLATE VI. Temperature Coefficients of Cu-Ni-Mn Alloys.

electric furnace. The metal as it came from the furnace was in the form of a cylindrical ingot about ¾ inch (2 cm.) in length by ½ inch (1.2 cm.) in diameter. A piece was taken from this ingot and rolled cold, with occasional annealing, to $\frac{1}{16}$ inch (0.15 cm.) diameter. This wire was drawn through steel dies to a diameter of from 10 to 20 mils. (0.25 to 0.50 mm.) Before measurements were taken the wires were annealed at a cherry-red heat, to reduce them to a uniform condition.

Resistances were measured by comparing the fall of potential across a known length of the wire and that across a Wolff

manganin standard connected in series with it. The resistance of each specimen was measured at six or seven different temperatures ranging from room temperature to 80°C. Readings of voltage were taken with a Wolff potentiometer to an accuracy of about one in fifty thousand. This degree of accuracy was necessary in determining temperature coefficients, since in this case the difference of two resistances was required.

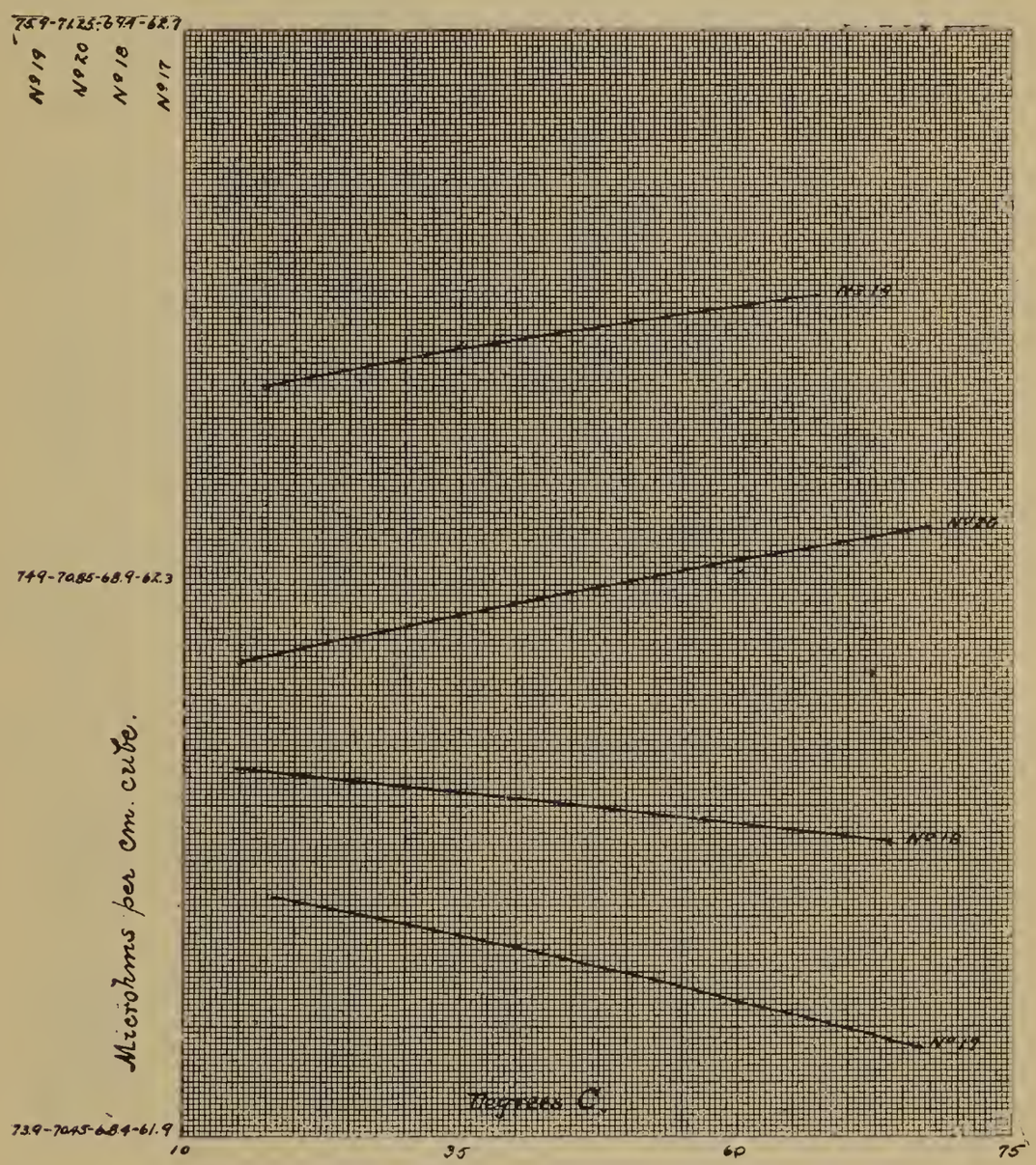

PLATE VII. Resistivity of Cu-Ni-Mn Alloys.

COPPER-NICKEL-CHROMIUM ALLOYS.

Four sets of alloys were made up, containing 5, 10, 15 and 20 parts of chromium, respectively, per 100 parts of copper plus nickel. A few specimens were made up later, containing 25 parts of chromium per 100 parts copper plus nickel.

The results of the investigation relating to the chromium alloys are given in Table I, and are plotted to co-ordinates on Plates I, II, III and IV.

TABLE I.

Specimen No.	Cu.	Ni.	Cr.	Microhms per cm. cube at 20° C.	Temp. Coeff. per deg. C. at 20° C.
41	10	90	25	107.	.....
39	16	84	25	111.6	.....
38	16	84	25	110.	.....
40	20	80	25	121.8	.....
1	0	100	20	96.9	0.00012
30	0	100	20	95.9	.....
32	5	95	20	98.3	.....
26	10	90	20	106.3	0.000079
28	10	90	20	106.4	.....
37	15	85	20	112.9	0.000078
29	15	85	20	109.8	.....
34	20	80	20	108.7	.....
2	25	75	20	86.3	0.00012
3	50	50	20	36.7	0.00031
4	75	25	20	21.3	0.00046
5	100	0	20	2.7	0.00299
6	0	100	15	84.1	0.00020
35	10	90	15	95.7	.....
33	15	85	15	99.0	.....
7	25	75	15	86.4	0.00011
9	75	25	15	22.1	0.00047
10	100	0	15	3.4	0.0025
11	0	100	10	67.8	0.00037
36	15	85	10	86.3	.....
12	25	75	10	83.9	0.00016
13	50	50	10	50.7	0.00018
14	75	25	10	22.4	0.00042
15	100	0	10	2.2	0.00349
16	0	100	5	45.7	0.00097
17	25	75	5	70.5	0.00041
18	50	50	5	55.1	0.00014
19	75	25	5	25.1	0.00035
20	100	0	5	2.1	0.00345

CONCLUSIONS.

1. The effect of the addition of pure chromium to pure copper was that the resistivity of copper was only slightly increased. The form of the curve resembled that for a eutectic alloy. This fact indicates that chromium is only very slightly soluble in copper.

2. The effect of the addition of pure chromium to pure nickel was that the resistivity of nickel was very greatly increased. The

form of the curve in this case indicates that nickel is capable of holding chromium in solid solution.

3. The effect of the addition of pure chromium to alloys of copper and nickel:

For any single Cu-Ni alloy the resistivity first rises and then falls off upon the addition of chromium. At a certain chromium concentration a maximum resistivity is attained for each Cu-Ni alloy, and as the concentration of the copper in the alloy increases, this maximum approaches the axis of zero chromium. These facts are clearly evident from a study of the curves on Plates III and IV.

4. The effect of the addition of chromium on the temperature coefficient:

In all cases, when the resistivity of an alloy was increased by the addition of chromium, the temperature coefficient was reduced. And when the resistivity was reduced the temperature coefficient was increased.

5. An alloy of very high resistivity (112 microhms per cm. cube) and of negligible temperature coefficient (0.000078) was found. This alloy would appear to have good commercial possibilities.

TABLE II.

Specimen No.	Cu.	Ni.	Mn.	Microhms per cm. cube at 20° C.	Temp. Coeff. per deg. C. at 20° C.
1	100	0	5	17.9	0.00017
2	80	20	5	33.5	0.00014
3	60	40	5	50.4	0.000089
4	50	50	5	55.1	0.000085
5	40	60	5	54.35	0.00022
6	30	70	5	50.72	0.00109
7	20	80	5	38.8	0.00239
8	0	100	5	17.4	0.00297
9	100	0	8	19.7	0.00032
10	80	20	8	40.2	0.000075
11	60	40	8	54.8	0.000071
12	50	50	8	58.1	0.000088
13	40	60	8	60.05	0.00014
14	30	70	8	55.8	0.00053
15	20	80	8	45.8	0.00185
16	0	100	8	23.3	0.00249
17	70	30	15	62.1	—0.000026
18	60	40	15	68.7	—0.000016
19	50	50	15	70.8	+0.000025
20	40	60	15	75.3	+0.000064

COPPER-NICKEL-MANGANESE ALLOYS.

Three sets of alloys were made up containing 5, 8 and 15 parts of manganese, respectively, with 100 parts of nickel plus copper. Table II gives the results of the investigation of these alloys and Plates V, VI and VII show the results plotted to co-ordinates.

CONCLUSIONS.

1. Within the limits covered by the investigation the addition of manganese to the alloy of copper and nickel at any concentration causes an increase in resistivity.

2. The generally accepted conclusion that an increase of resistivity is accompanied by a decrease of temperature coefficient is in general confirmed for the alloys of copper, nickel and manganese.

3. The curves obtained indicate that there is an alloy containing approximately 55 Cu, 45 Ni and 15 Mn, which has a resistivity of about 70 microhms per cm. cube, and a temperature coefficient of zero at 20°C. This alloy is a much better resistor than any of those used at the present time for precision apparatus.

ACKNOWLEDGMENT.

The authors express their sincere thanks to Dr. M. A. Hunter for his kind assistance in carrying on these investigations and for his many valuable suggestions.

Russell Sage Laboratory,
Rensselaer Polytechnic Institute, Troy, N. Y.
Feb., 1916.

DISCUSSION.

M. G. Lloyd (*Communicated*): The correct unit of electric resistivity is "ohms per centimeter cube," and not per cubic centimeter, as it frequently appears in this paper.

A paper presented at the Twenty-ninth General Meeting of the American Electrochemical Society, in Washington, D. C., April 27-29, 1916.

DETECTORS IN WIRELESS TELEGRAPHY.

By Wilder D. Bancroft.

Pierce[1] classifies the detectors used in wireless telegraphy under the following heads: electrolytic detectors, crystal rectifiers, coherers, magnetic detectors, thermal detectors, vacuum detectors. This paper deals with the first three cases, beginning with the electrolytic detector.[2] "The electrolytic detector for electric waves, as described by Fessenden and shortly after by Schloemilch, consists of a cell containing an electrolyte and having one electrode of very small area, usually in the form of an extremely fine wire of platinum, and as the other electrode a larger area of platinum or some other metal. When used in wireless telegraphy the two electrodes are connected in a circuit upon which the electric oscillations are impressed, so that the rapidly oscillating electric currents in the circuit are made to traverse the cell of the detector . . . . The electrolyte employed in the electrolytic detector is usually 20 percent nitric acid, though almost any electrolytically conductive liquid (dilute sulphuric acid, common salt solution, caustic soda, etc.) may be used. For a highly sensitive detector the fine platinum wire employed as the sensitive point may be as small as one or two ten-thousandths of an inch (0.0025-0.0050 mm.) in diameter. For a less sensitive detector, which is not so likely to be destroyed by strong signals, wire as large as one-thousandth of an inch (0.025 mm.) or even larger may be used."

The usual way is to polarize the detector cell by means of an external circuit. When the electrical waves strike the detector a current passes. This is a case of depolarization by electrical waves,[3] which tend to remove the adsorbed gas from the surface

[1] Principles of Wireless Telegraphy, 143 (1910).
[2] *Ibid.*, 201 (1910).
[3] *Cf.* Bancroft: Trans. Am. Electrochem. Soc., **29**, 309 (1916).

of the electrode, thus cutting down the over-voltage and the polarization.

In the crystal detector a crystal or carborundum or other suitable substance is wrapped or plated on one side with copper or platinum. A conducting point is brought practically into contact with the other side. When electrical waves pass, a better contact is made and a current passes. The gas film is removed more or less completely under the electrical stress, thus decreasing the insulation. Different points in the same surface of the same carborundum or molybdenite crystal show great differences in sensitiveness. This is probably due to localized impurities in the crystal. Similar differences have been observed in the thermo-electric behavior of the same crystals.[4]

"Some of the specimens [of molybdenite] are thermo-electrically negative with respect to copper while other specimens are thermo-electrically positive with respect to copper . . . The great variability among the specimens studied may be due to an admixture of small quantities of some other substance with the molybdenite, or it may be due to structural differences from point to point in the crystal. The differences in the specimens could not have arisen from the copper-plating or from the heat employed in soldering the junctions, because [four of] the specimens were tested before the copper-plating and soldering was done, and by means of the preliminary test were classified as positive, negative, positive and negative respectively, which agrees with the determination after soldering. The preliminary test was made by touching the specimens with two copper wires attached respectively to the two terminals of the galvanometer, one of the wires being slightly warmer than the other. *This preliminary test proved very interesting in that it showed that one may find, all over many of the pieces cut from a crystal of molybdenite, points where the substance is thermo-electrically positive and other points where it is thermo-electrically negative.* These positive and negative points sometimes lie so near together that, with a fine-pointed exploring electrode attached to a galvanometer and warmed by heat conducted from the hand, one may find the deflections of the galvanometer reversed from large positive values to large negative values on making the slightest possible motion

[4] Pierce: Principles of Wireless Telegraphy, 192 (1910).

of the pointer over the crystal. Explorations of this kind failed to show any definite orientation of the thermo-electric quality with respect to the crystallographic axes."

According to Pierce,[5] molybdenite, MoS_2, is the most sensitive of the crystal rectifiers thus far investigated. This is especially interesting because the experiments on ore flotation show that the sulphide ores have a marked tendency to adsorb gases. According to Wood,[6] molybdenite ores are now being concentrated by flotation.

Carborundum crystals show unilateral conductivity,[7] since "the current through the crystal in one direction under a given electromotive force was found to be different from the current in the opposite direction under the same electromotive force." In terms of our hypothesis this means that the thickness of the adsorbed gas film is decreased more when the crystal is charged positively than when charged negatively, or *vice versa*. This is not without analogy. Twomey[8] has shown that chloroform adsorbs air less readily in alkaline solutions where the chloroform is charged negatively by adsorbed hydroxyl ions than in acid solutions where the chloroform is charged positively by adsorbed hydrogen ions. I cannot agree entirely[9] that "when suitable crystals are employed, the crystal contacts are *detectors* for electric waves because they are *rectifiers* for rapid alternating currents." It is quite true that the crystals must conduct unilaterally if they are to be used as detectors without a battery in the local circuit; but this requirement is not necessary if a battery is used.

Since the action of the crystal detectors merely involves the temporary decrease in the thickness of the adsorbed gas film, it is not surprising that carborundum crystals should show little or no change with time when used as detectors or rectifiers.[10]

"In confirmation of the absence of electrolytic polarization, a durability test of the carborundum rectifier has been made as follows: A crystal of carborundum enclosed in a glass tube with a few drops of oil and held between brass electrodes, one of which was pressed forward by a spiral spring, was kept under

[5] Principles of Wireless Telegraphy, 178 (1910).
[6] Eng. and Min. Jour., **93**, 227 (1912).
[7] Pierce: Principles of Wireless Telegraphy, 164 (1910).
[8] Jour. Phys. Chem., **19**, 360 (1915).
[9] Pierce: Principles of Wireless Telegraphy, 175 (1910).
[10] *Ibid.*, 176 (1910).

almost daily observation[11] from October 23, 1907, until March 18, 1908. During these five months more than 1,200 measurements were made of the direct current obtained through the crystal under different direct and alternating voltages. The rectifier was kept in a temperature bath and was subjected to various long periods of heating and cooling ranging from 0° to 80° C. Notwithstanding the long continued exposure of the crystal to large changes of temperature, and notwithstanding the frequent loading of the rectifier with current, it was found at the end of the series that the values of the direct current obtained from the crystal under a given applied alternating voltage over a range of current from 4 to 400 micro-amperes (direct) and a range of voltage between 1 and 6 volts (alternating) did not differ from the corresponding values at the beginning of the series by an amount exceeding the limit of accuracy of the experiment, which was about ⅓ of 1 percent. This experiment shows that, if there is any kind of electrolytic action, it must be of such a character as to change the nature of the electrodes or of the crystal only very slowly, if at all."

In another passage Pierce[12] compares the electrolytic and the crystal detectors. "The resemblance of the oscillogram with the electrolytic detector to those with the crystal rectifiers is close, in so far as depends on the fact that both classes of rectifiers are nearly perfect [13] rectifiers when employed under their best conditions. The electrolytic rectifier, in order to approximate perfection[14] as a rectifier must be polarized by the superposition of a direct current; while the use of the direct current with the crystal rectifier does not always materially improve the rectification. Also *the two rectifiers are different, in that the electrolytic rectifier shows evidence of electrolytic polarization capacity, which, so far as may be judged from the oscillograms, is absent with the crystal rectifier.* The experiment with the electrolytic detector, since it shows in the matter of polarization capacity the inte-

[11] This series of measurements was carried out by Mr. K. S. Johnson, to whom the writer wishes to express his sincere thanks. The experiment was finally discontinued on account of the accidental melting of the cement holding in the end of the tube.

[12] Principles of Wireless Telegraphy, 212 (1910).

[13] A rectifier is called "nearly perfect" when the ratio of the current in one direction to that in the other is large.

[14] The current through the electrolytic rectifier is slightly asymmetric when no polarizing current is used.

grative action of this detector, which was sought for and not found with the crystal rectifier, is thus an interesting 'control' experiment. In the matter of sensitiveness the best crystal rectifiers are about equal to the electrolytic detector."

All the statements in the preceding passage are in accordance with the theory as outlined. While Pierce does not give the true theory of the electrolytic detector and the crystal detector, his conclusions in regard to the latter are interesting, especially in view of the fact that many people have believed that thermo-electric phenomena play an essential part. His conclusions follow:[15]

1. An examination of the characteristics of contact detectors using carborundum, anatase, brookite, hessite, iron pyrites, and silicon shows that we are dealing with the same kind of a phenomenon in the case of all these crystal substances. The various other crystal-contact detectors which I have not examined probably act in the same way.

2. At the contact between the crystal and a common metal, or between two different crystals, or between two apparently similar crystals, there is asymmetric conductivity, permitting a much greater current to flow in one direction than in the other under the same applied voltage.

3. These contacts all have a rising current-voltage characteristic.

4. These crystals all have a large thermo-electric force against the common metals, and the amount and direction of the thermo-electric force is different at different points on the crystalline bodies.

5. The rectifying effect is also different in amount and direction at different points of the crystalline body; the direction of the rectifying effect is often opposite to the effect that would be obtained by heating the contact.

6. Thermo-electricity does not explain the phenomenon of rectification; but the two effects, since both exist in such marked degree in the same bodies, may be related in that both may have their seat in some common property on the materials employed. *For example, if we suppose that a surface of separation between the crystalline body and some other body permits the passage of electrons more easily in one direction than in the other, this would*

[15] Pierce: Principles of Wireless Telegraphy, 199 (1910).

account for the rectifying effect, and would also account for the thermo-electric effect, provided the velocity of the electrons is suitably different at different temperatures.

7. The thermo-electric explanation of the rectifying effect, if we had found it to be supported by the experiments, would have correlated the phenomenon of rectification at a solid contact with the body of information that we already have in regard to thermo-electricity, but we should still have had by no means a complete knowledge of the action, because our knowledge of thermo-electricity is very incomplete.

8. From experiments with thermo-electricity we are familiar with the fact that the energy of an oscillatory electric current passing through a high-resistance contact is partially converted into heat energy, and that the heat energy so obtained, if produced at a thermal junction, is again partially converted into electric energy manifesting itself as a direct current. It is perhaps, after all, more simple to suppose the alternating current to be converted into direct current without the intermediation of heat; and this seems to be the case with the crystal contact rectifiers. This result opens up a new field for investigation, which may contribute to a better understanding, not only of thermal electricity, but of the much larger question of the mechanism of electrical conductivity in solid bodies.

Under coherers Pierce[16] includes only those detectors which employ a loose contact and require to be shaken, tapped or otherwise moved to restore the contact to its sensitive condition after the receipt of a signal. A great many modifications of the Branly coherer have been made, including the use of a single contact or a few contacts in series or parallel, between metallic balls or points to take the place of the filings.

"These various forms of coherer have their importance in the fact that, on the receipt of electric waves, a sufficiently large current is started in the local circuit to operate a relay, ring a bell, or give other form of alarm that can be heard at a distance from the operator's desk. Also the current permitted to flow in the local circuit of the coherers during the receipts of electric waves is sufficiently large to start machinery and control a mechanism (for example, a torpedo or dirigible craft) at a distance. This

[16] Principles of Wireless Telegraphy," 143 (1910).

kind of result is not easily attained with the other forms of detectors, which do not permit of the use of sufficiently large currents in the local circuit to sound an alarm or start electrical machinery. Thus the coherer, though lacking in sensitiveness to feeble waves and not now generally employed in the receipt of messages, has still a field of usefulness.

"Besides the filings coherer we shall describe here another interesting form of coherer—that devised in 1902 by Lodge, Muirhead and Robinson. This instrument consists of a small steel disc, rotated vertically by a clockwork, so that the disc is just separated from a column of mercury by a thin film of oil on the surface of the mercury. One electrical contact is made to the wheel through a brush, and the other connection is made to the mercury well through a binding post. The impulse of the electric oscillations breaks down the oil film and establishes momentary cohesion between the steel disc and the mercury. A current from a local battery passes through the disc and mercury contact, and operates a siphon recorder, which is used in series with the battery and the coherer. After the impulse ceases, the motion of the disc brings continuously a fresh oil film into the contact and causes de-coherence. The siphon recorder gives a written record of the dots and dashes of the message. A felt brush serves to keep the rotating disc free from dust before and after contact with the mercury.

"A generally accepted theory as to the reason for the coherence of the filings, or other form of imperfect contact used in the coherers, has not been established. I shall state briefly some of the views presented in explanation of the phenomenon. Before the arrival of the waves, the high resistance of the contact is generally supposed to be due to the presence of some kind of poorly conductive film at the contact. In the case of the Lodge-Muirhead coherer, the insulating film is evidently present in the form of a film of oil. In many of the coherers a poorly conductive film is present in the form of an oxide of the metal. This is evident from the fact that in some cases the metallic particles (*e. g.,* iron or steel) are artificially prepared by oxidizing them in order to make of them a good coherer. The poorly conductive film may also be present in some cases in the form of a sulphide of the metal. On account of the readiness with which many

metals (called the baser metals) enter into combination with the oxygen or sulphur dioxide of the air, a thin film or sulphide is always present on the surface of most of the baser metals, unless special care is taken to remove it.

"Apart, however, from the existence of such films of foreign matter at the contact, it seems not impossible that the high resistance before the arrival of the waves may be a property of the surfaces of even pure metals when these surfaces touch only very lightly. If we assume the presence of the poorly conductive film at the contacts of the coherer, we may suppose that, on the arrival of the electric waves, the poorly conductive film is removed by the heat developed by the oscillatory currents. This starts the local current which, developing further heat, still further improves the contact and permits the passage of further current. Instead of heat being the chief agency in removing the oxide or other poorly conductive film, or in bringing together the loose contacts, it may be that this is done by the electric attraction between the filings, which before the current starts will be charged with opposite signs of electricity, and which under the added electromotive force produced by the electric oscillations may attract each other strongly enough to pull the contacts together."

According to the theory advanced in this paper, the air film is the essential thing and the oxide film is more or less secondary. The thicker the oxide film is, up to a certain limit, the thicker will be the air film and the higher the voltage necessary to cut down the resistance markedly. That the conducting particles should cohere is not surprising. The only reason why two pieces of the same metal or two pieces of porcelain do not become one piece when pressed together is because of the adsorbed air on the surfaces. As Breuer[17] says: "All solids condense on their surfaces certain amounts of gases from the air and hold them with great force. The new surfaces, which are formed when a porcelain plate is broken, are covered instantaneously with particles from the surrounding atmosphere, and these are held in place powerfully as a thin, adherent elastic cushion. The portion of this layer which is next to the porcelain is believed nowadays to be as solid and dense as the porcelain itself, while the outer surface has the density of the air. A simple mechanical pressure, no matter how

[17] Kitte and Klebstoffe, 23 (1907); *Cf.* Bancroft: Jour. Phys. Chem., **20**, 3 (1916).

strong, is therefore not sufficient to bring the porcelain surfaces into intimate contact."

When the air film is removed more or less completely, the solid particles stick to one another more or less tightly and have to be separated by tapping, shaking, or other means. Depending on the conditions of the experiment we may have the oxide films coalescing or the metals themselves. If sufficient energy is expended at the contacts we may have fusion;[18] but this is not a necessary part of the theory. From this point of view the essential difference between the coherer and the crystal detector is that coalescence does not take place readily in the latter case and does in the former. Experiments on welding by pressure give independent confirmation of this fact.

While Robinson[19] gives quite a different theory of the coherer, it only calls for a slight change in the wording of his argument to make it applicable to the theory I have outlined. In connection with the action of the Lodge-Muirhead coherer it is interesting to note that Lenard[20] found, nearly thirty years ago, that mercury wets platinum only when a current is flowing. At other times there is evidently an air film.

Brown[21] superposed an alternating current on a cell, $Zn|H_2SO_4|C$, and found that the polarization was decreased thereby. "By making the surface of the anode in contact with the electrolyte small in area, the action of the alternating current will be concentrated and the ions will be correspondingly increased in chemical activity. In one case the anode was constructed of a fine platinum wire dipping about one-tenth of an inch into the dilute sulphuric acid and an external battery of two volts applied. When the alternating current was superimposed the platinum started to oxidize, and in a short time the whole of the wire in contact with the liquid was turned into a black powder. The same thing happened with gold, the wire turned into a yellow insoluble powder. With the filament of a carbon lamp as anode the carbon was completely dissolved or turned into gas; and, in fact, no conducting material could be found that would resist the combined

[18] Sundorph: Wied. Ann., **68**, 594 (1899).
[19] Drude's Ann., **11**, 770 (1903).
[20] Wied. Ann., **30**, 212 (1887).
[21] Proc. Roy. Soc., **90** A, 26 (1915).

action of the two currents when applied in this concentrated manner.

"These experiments were carried out with alternating currents at a frequency of 12,000 periods per second, as it was thought that the stimulating effects were much greater at high frequencies, but no tests were made to prove this point. * * * The function of the alternating current is to stimulate the chemical changes, it may be to produce oxidation as in the foregoing experiments, or in other cases it may be to reduce the oxide, although no direct test was made to prove this supposition.

"I think that these experiments explain the action of the Branly filings coherer—a device in which the group of granules act normally as an insulator, but become conductive when high-frequency currents such as Hertz waves pass through them. Iron or nickel filings are insulated from each other by a thin film of oxide, but the coherer has a small capacity, with the oxide as dielectric, and the waves are thus allowed to pass. The rapid alternating currents act upon the oxide dielectric and, by stimulating chemical action reduce the oxide at the points of contact to a metallic or conducting form and allow a continuous current to flow. When the tube is shaken the oxide again intervenes and another application of the alternating current is required to produce conduction."

There is a charming vagueness about the words "by stimulating chemical action, reduce the oxide." Also one would have liked to know just what the "insoluble yellow powder" was which was obtained from a gold electrode. From the context one would suppose it to be an oxidation product of gold; but the properties are more like those of disintegrated gold.

CONCLUSIONS.

The general results of this paper are:

1. The coherer, the electrolytic detector and the crystal detector act as they do because an electrical stress decreases the thickness of the adsorbed gas film and therefore decreases the resistance.

2. The unilateral conductance of the crystal detectors is essential when there is no battery in the local circuit; but it is of no theoretical importance when a battery is used.

3. The essential difference between the coherer and the crystal detector is that coalescence takes place readily in the first case and not in the second.

4. It is not necessary that the oxide film of some coherers should be removed by the current, though this may happen.

5. In the crystal detectors the marked changes in the behavior of adjacent portions of the same crystal face are probably due to localized impurities.

Cornell University.

DISCUSSION.

President Addicks: It seems to me that Dr. Bancroft has broken his own rule by going into a very practical field. He is finding some explanation for flotation, which is a matter that is worrying a great many people at the present time. He also explains the nature of a contact resistance in a busbar joint. If we take two busbars and bind them together there is a resistance there which is ohmic in character, and is diminished by pressure, which, I suppose, is thinning the layer of air; it is also diminished by moisture, which would certainly alter the character of the film.

In the paper it is stated that the only reason why two pieces of metal or porcelain do not become one, when pressed together, is the presence of this film, and the point is made, if I understand the paper correctly, that it is not oxide, but gas. Would there not be an objection to that in the case of gold leaf, which the dentist uses in filling a tooth. He has to make a perfect weld in the cold, and gold is one of the few metals that is practically free from oxide film. Is not that the reason why it can be so welded, while other materials cannot?

The other extreme would be blue powder or zinc, where there is a film in oxide and no cohesion at all. Is Prof. Bancroft arguing against the gas idea and in favor of the oxide idea?

W. D. Bancroft: I do not mean to go to extremes and say that no metals oxidize. It is perfectly possible that in a good many of these cases we do have films, but as a matter of fact we know you can improve the work of the detector in some cases either by

oxidizing the surface, or converting the surface of a crystal into a sulphide, and the thing which produces most of the resistance, or at any rate which produces most of the changes in the resistance, is the adsorbed gas film, which may be adsorbed on the metal or oxide surface, or sulphide surface, or any other surface you may happen to have. The welding of gold is due in part to the fact that you have no oxide film, and due also to its very great ductility, because, as a matter of fact, you can take any metal, in crystalline or powdered form, and if you put it under sufficient pressure you will get a perfect weld, because under those conditions you squeeze out the air film that there is around it. We all know that with nickel and aluminum and things of that sort there is always an oxide film on the surface, but the oxide film can also absorb air, and in the case of the crystal detector you do not start with the metal, but with the sulphide, or carborundum, or whatever the thing may consist of.

Irving Langmuir: Dr. Bancroft's explanation of the action of wireless detectors applies very well, I think, to the coherers, but it seems very unlikely that it can account for the phenomena observed with crystal detectors.

In detectors such as the galena detector (a crystal of galena with a piece of brass wire pressed against it), there is rectifying action when alternating potentials are applied. The effect may be observed with potentials of almost any frequency, and does not vary greatly with the frequency. According to Dr. Bancroft's theory, we should have to assume that the adsorption films are at least in large part partly formed and destroyed during each cycle of the alternating current. It is inconceivable that such actions could take place a million times per second with nearly the same facility as with lower frequency. In the coherer, on the other hand, when the film is once broken down, the conductivity of the contact becomes and remains enormously greater than before.

A more probable explanation of the action of crystal detectors is that the rate at which electrons can pass from one substance into another is limited. An analogy in another field will help to illustrate my meaning. It is usually considered that a solid body dissolves in a liquid at a rate which depends on the diffusion of the dissolved solid through a film of liquid adhering to the surface.

Thus if a piece of gypsum is placed in water and the solution is stirred, then according to the Noyes-Whitney theory the layer of the solution in actual contact with the crystal is saturated with the salt. The rate of solution is then limited by the rate at which the salt can diffuse away. It is often taken for granted that the crystal would dissolve extremely rapidly if its surface could be kept in contact with pure water. I expect to show (in a paper soon to be published) that this is often a fallacy.

In the analogous case of a substance evaporating into a very high vacuum, we find that the rate of evaporation never exceeds a certain definite limit at a given temperature. This rate may be readily calculated by the equation

$$m = \frac{M}{2 \pi R T} p$$

where m is the rate of evaporation in grams per sq. cm. per second, p is the vapor pressure of the substance, and M is the molecular weight. Thus mercury evaporates in a vacuum only slowly at room temperatures, and at a rate which cannot be increased by improving the vacuum. I expect to show that this same equation may be applied to the maximum rate of solution of solids in liquids.

The emission of electrons from heated metals is an analogous phenomenon. At a given temperature the number of electrons emitted is perfectly definite and is not appreciably increased by the application of ordinary external electric fields. If, however, extremely intense fields are produced, such as may be obtained when two surfaces at slightly different potentials are brought into contact, then we should expect that currents could be obtained even at room temperature, and that the magnitude of these currents would depend on the applied potential difference. Under such conditions, if the contact is formed by two dissimilar substances having different electron emissions, it is natural that the current should flow more easily in one direction than in the other. I hope soon to develop this theory of crystal rectification in more detail.

A paper read before the New York Section of the American Electrochemical Society, in Joint Session with the Illuminating Engineering Society, November 11, 1915. Called up for discussion at the Twenty-ninth General Meeting of the Society, in Washington, D. C., April 27-29, 1916.

UNSTABLE STATES IN ARC AND GLOW.

By W. G. Cady.

In solid and liquid conductors, in which Ohm's law is applicable, unstable states, where a small variation in voltage produces a large change in current, are almost unknown. Exceptions occur only when a critical state in the conductor is reached, as for example in an iron wire at a certain temperature, or in an aluminium valve cell at break-down voltage.

Characteristics of the gas discharge.—When an electric current passes through a gas, the number of available carriers of the discharge may increase with increasing current at a very rapid rate. In a popular sense, an ionized gas is a most "unstable" conductor, having a resistance by no means amenable to Ohm's law. In the language of dynamics, however, a gas discharge is normally stable in the sense that there is a restoring force to damp out small disturbances. The nature of this force, as well as the criterion for stability of any discharge, can be understood best by reference to the characteristic curve of the discharge, as shown in Fig. 1. This curve shows qualitatively the relation between current and voltage in the discharge between two fixed electrodes. The nature and pressure of the surrounding gas are supposed constant, except as modified by conditions at the electrodes themselves. All of the common types of discharge are represented on this diagram. With a sufficiently high e. m. f. it is theoretically possible, by decreasing the external resistance, to pass through all the stages in succession. Practically, certain portions are unattainable, and different sources of supply are necessary for different forms of discharge. In any case, however, the curve is characteristic of the discharge apparatus and not of the supply.

The first part of the curve, OA, represents the extremely minute saturation current, which soon assumes a value that is practically constant over a great range of voltage. This current is carried

by the few free ions that are always present. As the voltage increases, the charged particles are sufficiently accelerated to form new ions by impact. At this point the current begins to increase,

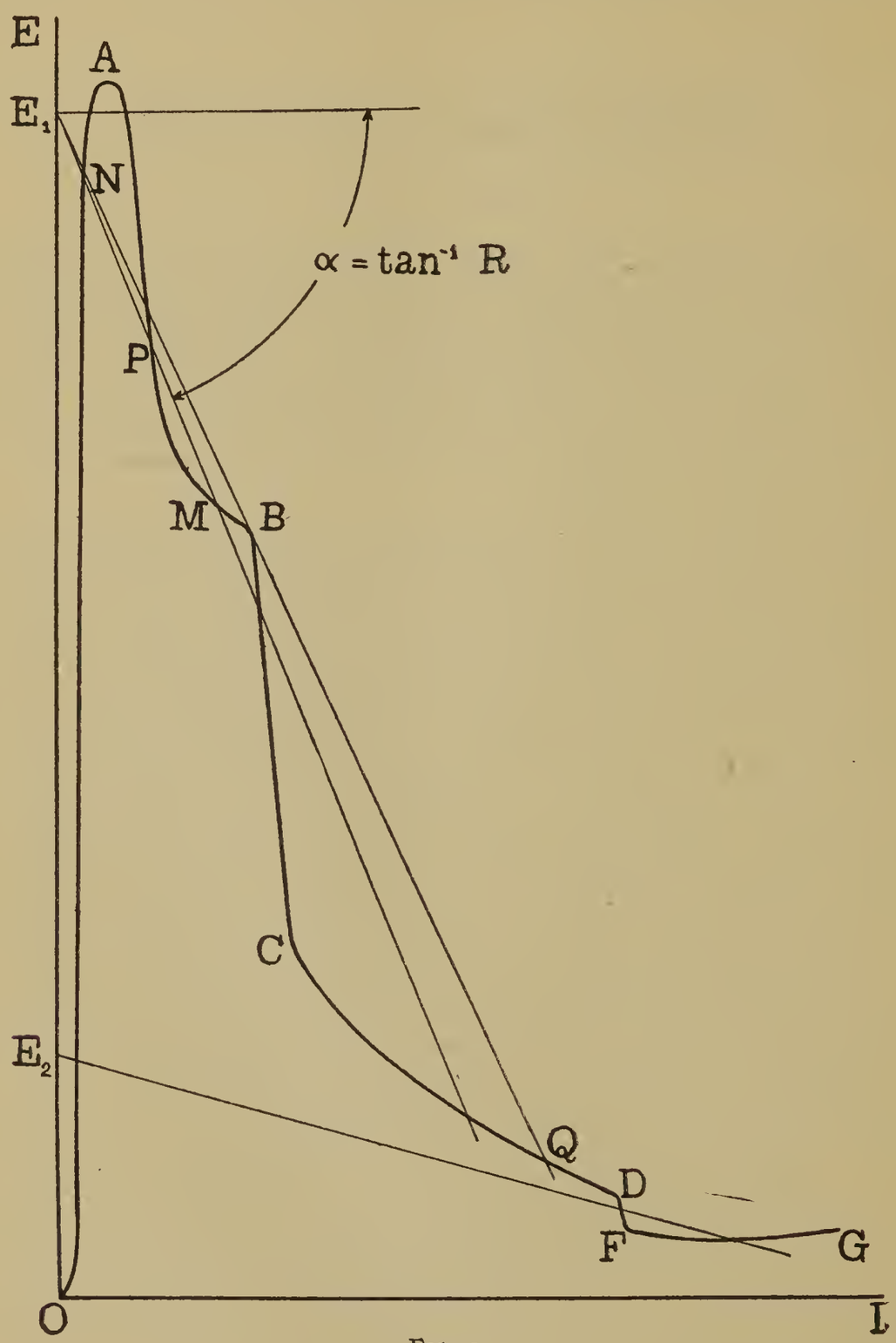

Fig. 1.

and a faint glow appears. The point *A* represents the sparking potential. In the present case the external resistance is supposed to be too high to admit of sparking.

AB is the glow discharge proper, in which the rate of ionization is so great that the voltage across the gap falls rapidly with increasing current. If the cathode is small, the curve may rise again before *B* is reached, owing to the abnormally high cathode drop.

Since the drop in potential at the cathode is much larger than that at the anode, the cathode becomes relatively hot. As *B* is approached, the expenditure of energy at the cathode becomes so high that the cathode rapidly becomes incandescent. Here a new phenomenon appears, namely, the emission of electrons from the hot cathode, according to Richardson's law. These greatly increase the ionization close to the cathode, and the positive ions thus produced heat the cathode by impact still more. At a point depending upon the volatility of the cathode, the latter begins to vaporize, thus decreasing the cathode drop as well as the resistance of the gas. The discharge then quickly resolves itself into an arc, in which the negative base is concentrated to an intensely bright spot, the current is carried chiefly by the vapor from the cathode, but the mechanism of the discharge is essentially as before, except at the surface of the cathode. The portion *BC* of the curve cannot be observed. Over *CD* the discharge is an arc as far as the cathode is concerned, but since less energy is being expended at the anode, at the latter we may still have a glow discharge. The positive base of the discharge is still diffuse and faintly luminous. This is the *first stage* of the arc. Under ordinary circumstances the first stage may be difficult to obtain, since the arc at the anode often begins at the same time as at the cathode.

With increasing current the anode is brought to the boiling point. This causes a decrease in the anode drop and a further increase in conductivity of the gas, so that the portion *DF* is quickly passed over. *FG* is then a full arc, or *second stage* arc. Exceptions to this typical sequence of events will be described below.

Quantitatively it is impossible to make the diagram give a correct idea of the voltage and current relations, since the current at *G* is in reality many thousand times greater than at *A*.

Stability of the discharge.—While theoretically it is possible to maintain a steady discharge at any point of the entire curve, practically the transition from one portion to the next is always discontinuous. As the voltage or the external resistance is varied,

a critical point is always reached where the discharge is absolutely unstable, changing abruptly to a stable region on another part of the curve. Still, with any given supply e. m. f. and external resistance, it is always possible to predict between which two points the discharge must change. The method of procedure is largely due to Kaufmann.[1]

Let us suppose that the supply e. m. f. is measured by OE_1 in the figure. If M is the point on the curve at which the discharge takes place, then since the ordinate of M is the voltage consumed by the discharge, it is evident that the external resistance R is equal to tan α. If R is decreased, α must decrease and M will move to the right along the curve.

Kaufmann showed analytically that a stable discharge is only possible when the line through E_1, or the "resistance line," as it is called, *slopes more steeply than the characteristic curve* at the point in question. Thus the discharge is stable at M, and, starting with zero current, it would also be stable at N with the same external resistance, but not at P. A glow at P could only be obtained with an enormously high e. m. f. At B the discharge is unstable; this is the first of the unstable states to which attention is directed. As soon as the point of tangency is reached, the discharge changes abruptly to a first-stage arc at Q. If now the external resistance is increased, the discharge does not change back to a glow along QB, but owing to the vaporization of the cathode it remains an arc until the point of tangency at C is reached. Then, if, as is usually the case, the discharge cannot change to a stable glow, it goes out.

Similar points of instability exist at D and F. If the supply e. m. f. is low, as at E_2, not even the first stage of the arc is possible, but only the second. This is the case with most arcs, operating with low e. m. f. and small external resistance, and lighted by touching the electrodes together.

The physical significance of Kaufmann's criterion may be seen from the following considerations: if the resistance line slopes more steeply than the characteristic curve, then if through any chance the discharge at a given instant happens to take place at an abnormally high current, it cannot persist at this current, since the voltage available for the discharge is limited by the external

[1] Kaufmann: Annalen d. Phys., 2, 158 (1900).

resistance, and the steep slope of the resistance line brings the operating point too low for the increased current to be maintained, hence the current settles back to its normal value. Similar reasoning will show that if the resistance line slopes less steeply than the characteristic curve, then any slight disturbance will grow until the discharge goes out or becomes stable at another part of the curve.

In a general way this sort of stability is of course analogous to the mechanical stability of a pyramid, which is stable or unstable according to whether it stands on its base or is balanced on its point. A more exact analogy would be furnished by a hydraulic model, in which the discharge tube was represented by a valve so contrived as to open wider the greater the flow of water through it. This would provide the "falling characteristic."[2] If then the water were supplied from a vessel of variable height, and regulated by a valve at the supply, it is evident that at high pressure and with supply valve (external resistance) nearly closed any given flow of water would be maintained more stably than if the pressure were low and the supply valve wide open, for in the latter case a much greater percentage of the total "resistance" would be in the valve of "falling characteristic."

Kaufman applied his criterion of stability with great success not only to glow and arc, but to the point discharge, to a discharge gap ionized by an external source, and most remarkable of all, to the case of a discharge having a capacity in parallel with it. This came pretty near to being the discovery of the singing arc, which by a coincidence was discovered experimentally by Duddell in the same year.

By applying Kaufmann's criterion to Mrs. Ayrton's equations for the arc, Rasch[3] has deduced expressions for maximum and minimum length for stability, also for the critical external resistance and the maximum permissible drop across the arc for any given supply voltage.

The carbon arc.—I have obtained a glow discharge and both stages of the arc between carbon terminals, using an e. m. f. of 460 volts, in nitrogen at reduced pressure. Air was then admitted and the current increased until the hissing state was also reached,

[2] A valve of this sort has been described by Duddell: Proc. Phys. Soc., London, **26**, 117 (1914).

[3] Rasch: Electric Arc Phenomena, New York, 1913.

making four forms of discharge with the same electrodes. To accomplish this, however, it was necessary to vary the composition and pressure of the gas. On the characteristic curve for carbon electrodes the hissing point would be represented by a kink similar to that at *DF* in Fig. 1, but situated between *F* and *G*. The laws governing the current-voltage relations on transition between normal and hissing carbon arcs are the same as those discussed above.

First and second stages of arc. Effect of impurities.—The unstable state occurring between the first and second stages of the arc has been investigated by Arnold and the writer.[4] It is on the first stage that the ordinary mercury arc burns, having an anode of iron or graphite. The change from first to second stage has now been observed with anodes of a large number of metals, though in some cases reduced gas pressure or exclusion of oxygen was necessary.

An instability in the discharge is sometimes occasioned by traces of impurities on the surfaces of the electrodes. It is well known that the glow tends to change to an arc more readily if the metallic cathode is contaminated with traces of oxid. This is related of course to the emission of electrons from hot oxids. At the anode in a glow or a first stage arc, traces of impurities serve as nuclei around which the discharge tends to become concentrated, though it is still a glow. This effect may become so pronounced as to be taken for a new type of discharge,[5] especially since the voltage suffers a sudden drop when the concentration sets in. The effect is probably due to the poor heat conductivity and consequent high temperature of oxids and other compounds.

An unusual type of arc.—A very unusual type of discharge is that in which, as the current increases, an arc appears at the anode while there is still a glow at the cathode. Those who define the arc as essentially a cathode phenomenon will not be disposed to admit that this is an arc at all; yet it has every characteristic of an arc at the anode, and the appearance here does not alter further when the arc phase sets in at the cathode. The writer has encountered this form of discharge with anodes of C, Ag, Cu, and Hg, the cathode in most cases being of silver.

[4] Amer. Jour. Sci., **24**, 383 (1907).

[5] Hagenbach: Phys. Zeitschr., **12**, 1015 (1911); *cf.* Cady, Phys. Zeitschr., **14**, 296 (1913).

Is an arc possible from a pure metal?—The writer observed some years ago that a cathode of pure silver may become heated by the glow discharge in nitrogen nearly, if not quite, to the boiling point without the formation of an arc. The cathode was in the form of a small button of metal, resting in a shallow cavity on a carbon post, or better, on a plate of refractory material. In the latter case alundum was found most suitable, and the current was led up to the silver through a small rod of tungsten projecting through a hole in the center of the plate. Thus only the silver was exposed to the discharge, which took place in nitrogen or hydrogen at various pressures up to atmospheric. The anode was generally of tungsten. So little heat was conducted away from the silver cathode that it melted in a few seconds with a current of a few tenths of an ampere. A gradual increase in current caused the silver to become brightly incandescent and to vaporize copiously.

At currents as high as 1.3 amperes the discharge is still a glow, though the molten metal is white hot and vaporizes so intensely that clouds of silver "steam" fill the discharge tube. This is important evidence that incandescence and vaporization of the cathode are not enough of themselves to cause the formation of an arc. Whether even at the boiling point of silver the glow would still persist if no impurities were present cannot be stated. In the present tests, at the highest currents the cathode mantle always grew so large as to encroach upon the fringe of impurities that inevitably surrounded the molten mass, and then an arc immediately formed. The admission of a small quantity of oxygen also precipitated an arc.

Similar results were obtained with copper and with iron. Of chief significance is the fact that in no case was an arc seen to form at the clean surface of a molten metal. On melting, whatever traces of impurity were in the metal floated to the surface as a minute slag, and were driven to the extreme edges of the globule by the action of the discharge. Thus the part of the molten cathode immediately under the discharge was extremely smooth and pure. It was evident that the formation of an arc was rendered very difficult, to say the least, when the cathode was in this condition.

This fact has, I think, a bearing on the elusive and much dis-

cussed theory of the arc. The two most fundamental properties of the arc may be said to be the concentration of the discharge, and the diminished drop in potential at the cathode. Vaporization of the cathode and the conduction of the current by this vapor may be purely secondary phenomena, although generally present to a marked degree, and, I think, always present to some extent. It is possible that in order for the concentration to take place there must be some irregularity on the surface of the cathode, for example a roughness, if the cathode is solid, or else a trace of some foreign substance. This would then be analogous to the action of dust particles in producing the condensation of saturated water vapor. The writer hopes to investigate this subject further.

Intermittent discharge. Corona.—Both glow and metallic arc, as well as the discharge from points, are sometimes found to be intermittent. For this to be the case, the current must be relatively small and the capacity of the external circuit considerable. There is usually a certain critical external resistance at which the intermittance vanishes, as shown by the cessation of sound in a telephone connected to the circuit. The phenomenon is closely related to the use of the arc as a generator of electric oscillations. The Cooper-Hewitt mercury interrupter is a notable example of intermittent arc.

In a strong magnetic field an arc can also be made intermittent. In this case the instability is due to the lengthening of the column of vapor by the magnet, causing the voltage to rise above the point where the discharge can be maintained. Owing to the incandescence of the cathode, the discharge quickly relights and the operation repeats itself. The "ripping" sound sometimes produced when the arc formed on opening a switch is blown out by a magnet is doubtless an instance of this.

The corona discharge from high voltage transmission lines is similar to a glow discharge, and is said to be often intermittent. It exhibits the characteristic cathode and anode phenomena, as well as the tendency to concentrate at certain points which was mentioned above. Since the air serves as one electrode, the corona has in some respects more in common with the discharge from points and the brush discharge than with the typical glow, and as such it falls outside of the scope of this paper.

Rotations at the anode.—Two effects will now be described, illustrating the instability of gas discharges at certain currents. The first of these has to do with the anode, the second with the cathode.

In the iron arc in free air the discharge normally takes place between globules of molten oxid. The second stage sets in at a little over an ampere. A close examination shows that the bright spot at the positive end of the arc is in rapid rotation, describing a minute ring. As the current increases this form of rotation suddenly changes to one in which the ring is still smaller, then at about 1.8 amperes a large ring takes its place, which at a slightly larger current is replaced by a smaller ring again.

Each of the four types of rotation has its characteristic diameter and angular velocity, and produces a faint note of a certain pitch. Oscillograph records show that the current and voltage undergo corresponding periodic changes. After the current has gone beyond five amperes, the rotations cease.

The anode globule on cooling is found to consist of magnetic iron oxide, $FeO.Fe_2O_3$. This oxide is known to possess a complex structure, and to undergo changes in its physical properties at certain critical temperatures.[6]

Walden[7] found Fe_2O_3 to be stable in air up to about 1350°C., at which temperature it dissociates into O and Fe_3O_4. Kohlmeyer,[8] on the other hand, assigns to the melting point of Fe_2O_3 the value 1565°, with transition points at 1300° and 1035°. Hilpert[9] calls attention to the influence of previous history and method of treatment on the dissociation temperature of Fe_2O_3, while Wüst[10] asserts that at 1050° the compound $FeO.Fe_2O_3$ is formed, at 1100° $2FeO.Fe_2O_3$, and at 1200° $3FeO.Fe_2O_3$. According to Hilpert, Kaufmann identified also $2FeO.3Fe_2O_3$. I know of no investigations on the reactions that take place at higher temperatures than these, but it seems not improbable that still others occur before the final reduction of the iron is accomplished. In addition, there is the possibility of the formation and dissociation of a nitride.

[6] Heaps: Phil. Mag., **24**, 813 (1912). Somerville: Phys. Rev., **34**, 311 (1912). Koenigsberger: Phys. Zeitschr., **13**, 282 (1912).

[7] Walden: Jour. Amer. Chem. Soc., **30**, 1350 (1908).

[8] Kohlmeyer: Metallurgie, **6**, 323 (1909).

[9] Hilpert: Ber. Deutsch. Chem. Ges., **42**, 4893 (1909).

[10] Wüst: Metallurgie, **5**, 11 (1908).

As to the temperature of the oxid at the positive base of the arc, I can only say that it is well above the melting point of platinum. In other words, it is far above the range over which anything is definitely known about the composition of the oxid. Nevertheless, there are strong grounds for believing, as has been shown elsewhere,[11] that the oxid at the positive base of the discharge is more completely reduced than in the region surrounding, and that the potential drop close to the anode is consequently higher than at other points in the neighborhood. It is the effort of the discharge to take place from regions of lower potential drop that furnishes the propelling force for the rotations. The changes from one type to the next are probably due to modifications in the composition of the oxid, brought about by increasing temperature. I have found similar effects to a slight extent in nickel and cobalt. These results have a bearing on the use of the iron arc as a wave-length standard in spectroscopy.

Glow-arc oscillations.—The effect at the cathode to which reference has been made is of the nature of a rapid pulsation back and forth between glow and arc. To obtain it, the supply e. m. f. must be high, and the gas should be hydrogen at atmospheric pressure, mixed with a little hydrocarbon vapor. The electrodes may be of any metal, placed very close together, the discharge current being of the order of one-tenth ampere.

When the discharge is a glow, a spot on the cathode becomes heated to such a degree that a small arc forms; but the voltage then drops so much, and the current increases so little, owing to the shape of the characteristic curve, that the energy is too slight to maintain the arc, and immediately the glow sets in again. Such pulsations between arc and glow are of a frequency anywhere between 1 and 250,000, depending on various conditions. I have succeeded in converting 66 percent of the power applied to the discharge into high-frequency oscillations of this type. Unfortunately, the nature of the discharge is such that the conversion of large amounts of power by this means is impossible.

In these experiments no capacity was connected in parallel with the discharge, though the adjacent parts of the circuit acted as capacities for the high-frequency currents.[12]

[11] Phys. Rev., 2, 249 (1913).

[12] An account of these experiments will be found in Amer. Jour. Sci., 28, 89, 239 (1909).

The singing arc.—In the singing arc, including the Poulsen arc used in radio-telegraphy, a capacity and self-inductance in series are placed in parallel with the arc. The effect of the capacity is to drain energy from the arc when the current in the condenser circuit is in one direction, and to strengthen the arc current when in the other direction. Continuous oscillations are thus maintained, the condenser circuit receiving energy and timing its own impulses in a manner analogous to the balance wheel or pendulum of a clock.

The point of chief interest here is that, as Kaufmann, Simon and others have shown, such oscillations are possible only when the arc (or glow) possesses a falling characteristic. Simon has found that the alternating current or "dynamic" characteristic differs from the direct current or "static" characteristic, the difference being due to a sort of hysteresis, and that the result of this is that at high frequency the dynamic characteristic tends to change from a falling to a rising type. This limits the attainable frequency, but by reducing the hysteresis and choosing such conditions as will make the characteristic fall as steeply as possible, frequencies of over a million are easily reached.

If the oscillations are weak, the direct current through the arc simply fluctuates. This can occur with the carbon arc. If the oscillations are stronger, they put the arc out at each cycle, and before the arc re-lights the condenser becomes charged. The oscillating arc used in radio-telegraphy is of this type. A third type, in which the oscillations are powerful enough to make the arc re-light in the opposite direction, produce a coarse tone and are not much used.

Effect of second harmonic.—When the oscillations are of the second type, extinguishing the arc at each cycle, the wave form is very complex. The second harmonic is often prominent. As an example of oscillations of this type, of audible frequency, the following experiment may be described.

A carbon arc is made to sing, by connecting a large capacity and a self-inductance coil of low resistance in parallel with it. A second coil is connected to a capacity such that the natural period of the secondary circuit is nearly the same as that of the circuit connected to the arc. When the two coils are brought near together, the pitch of the arc changes, owing to the effect

of close coupling. If the pitch falls, it can be made to reach an unstable value from which it suddenly jumps up a whole octave, the discharge remaining stable at this higher pitch.

The probable explanation of this is, that when any two oscillating circuits are closely coupled, there are two possible frequencies, one higher and one lower, in either of which oscillations may take place. At a certain stage of coupling, the higher frequency is just an octave above the lower. If now the arc is on the lower frequency and has a very strong second harmonic, then if resonance is also possible at the octave above, the harmonic may be reinforced to such an extent as to assume the rôle of fundamental frequency itself. The pitch then rises to the higher octave.

SUMMARY.

The characteristic curve of a gas discharge is first discussed, with particular reference to the points of instability and to the condition for a stable discharge at any current.

Experiments on the different forms of arc, using carbon or metallic electrodes, are described. The effect of impurities on the electrodes is shown to be a concentration of the discharge. A type of discharge is described in which there is an arc at the anode though a glow at the cathode.

Under certain conditions a metallic cathode may become so heated by the discharge that it vaporizes freely without the formation of an arc. This is shown to have a bearing on the theory of the arc.

Intermittent discharges, rotations in the iron arc, "glow-arc" oscillations, and the singing arc are considered in the light of the characteristic curve and of the conditions for stability. A peculiar effect of harmonics in the singing arc, using coupled circuits, is described.

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DISCUSSION.

W. R. Mott: Mr. Cady has given us an excellent paper on what causes arc instability. In practical work we endeavor to study what causes arc stability. The two questions are closely related, however.

Mr. Cady says, "With respect to practical conclusions, the following may be said: for stability an arc should be operated with supply electromotive force, external resistance, and current all large." The stability of the arc is of great practical importance because of the inherent losses in the external circuit in series with the arc. An alternating-current lamp's stability is secured by the use of induction coils, without undue loss of efficiency except that resulting from decreased power factor on the line and hence decreased utilization of the electrical equipment. Also in series arcs the regulation is easily accomplished with little trouble or less of power. It is on the direct-current multiple-arc lamps that most energy is wasted in external control. In some old open-arc carbon lamps on direct current, as much as 40 percent of the total energy may be used in the controlling resistance. With flame carbons in an inclined-trim lamp as much as 45 volts can be used at each of two arcs in series on a 110-volt line, with perfect satisfaction as to arc stability. This makes an expenditure of less than 20 percent of the total energy in external control. This stabilizing action is partly secured by the magnetic action of a field controlled by the arc current, and its effect on an arc with increased current. This action stretches the arc, tending to increase its real resistance and hence to decrease the rate of increase of the current.

If you have a 220-volt circuit you get a more stable arc than on the 110-volt circuit. If you have a large external resistance you will get a more stable arc than if you have a small external resistance. And if you have a current of 1,000 amperes the external control needed is only 5 to 10 percent, whereas if you have only one or two amperes the external control may require 50 percent of the energy.

In connection with multiple-flame arc lamps, the question of the energy wasted in the external circuit becomes vitally impor-

tant. With flame carbons in the arc lamps as much as 45 volts at each arc can be used (with two arcs in series) on a 110-volt line. This makes an 85 percent energy utilization on a multiple circuit, which is very good.

The external control can also be arranged to have a more corrective characteristic than the usual resistance. This has been done in Nernst's lamps, where a sharp control is secured by using a fine iron wire coil in a vacuum. As this heats, it greatly increases in resistance, so with a small change in current there is a corrective factor for the glower which has a characteristic similar to that of the arc.

The importance of air currents on the stability of the arc is most marked. Inclined electrodes increase stability and power factor for this reason.

The use of four arcs in series on 220 volts is a great stabilizing factor. Four arc lamps in series on 220 volts or two arcs in series on 110 volts have been increasingly used in the last year in the design of some flame carbon lamps. There are six or seven new arc-lamp companies which have designed flame lamps with two arcs in series in the same lamp, using about 45 volts each on 110-volt line. The efficiency of power utilization in such a case is very great. The single flame arc is operated at 60 or 75 volts, whereas with the two-flame arcs in series the total voltage is 90 or 95 volts.

Again, it is possible to so proportion the several chemicals that with an increase in current there is a much better volt-ampere characteristic curve than is possible with the pure carbon arc. The power factor is also greatly improved. Another advantage of the flame arc is its low starting and operative voltage which can be half that of the pure carbon arc and the rate of increase in arc length is more than twice as good as with the carbon arc. These features make the flame arc ideal in the sense of giving a new region of stability to the arc and in the ability to throw more power into the arc.

W. C. Moore: In addition to Mr. Mott's discussion, there are two things which have occurred to me on hearing Professor Cady's very inspiring paper. About a year and a half ago there appeared in *Metallurgical and Chemical Engineering* an article

on the "Vosmaer Phenomenon." This consisted of a discharge between nickel wires forming the secondary terminals of an induction coil. If you examine them critically, I think that Professor Cady's results will explain how that particular discharge occurs. In that discharge, if the cathode is of smaller nickel wire than the anode, we find that the cathode glows rather brightly, and gives out quite an intense light. Now, according to Professor Cady's paper there is an unstable state between the glow and the arc, in which we have electrons emitted from the cathode, ionizing the gas in the space between the cathode and the anode. The positive ions formed in this way bombard the cathode, raising the temperature of the cathode, and the cathode begins to glow. It so happens that the heat conductivity of nickel, according to some recent work done at the University of Wisconsin, decreases as the temperature rises. It is also true that nickel-oxide is less volatile than nickel, and so we have in this case, when the cathode begins to glow, a little globule of molten nickel contained in this shell of highly emissive nickel-oxide, and the arc-glow, or whatever you want to call it, results, the metal not volatilizing to any great extent.

Professor Cady also brings out the point that in some cases an arc is impossible unless we have chemical reactions taking place between the electrodes, and that brings to my mind the controversy which has been going on between Richardson and Pring, on the cause of the thermal ionization of carbon. Pring asserts that the thermal ionization of carbon is always due to the impurities in the carbon, while Richardson has said that it is a pure thermal ionization. I am not so familiar with all the details of that as I might be, but Richardson asserts that Pring's results with purified carbons, in which his ionization current decreased, were not caused by the purity of the carbons, but by the magnetic effect of the high current used. That is a thing that we ought to think about. It seems that Professor Cady's results point at least in the direction of confirming Pring's results. Personally I am rather inclined to Pring's view.

G. M. J. Mackay: From observations on arcs operating as rectifiers in various gases between tungsten electrodes, we have come to the conclusion that rapid evaporation of the cathode and chemical reaction at the metal surfaces are not important factors

in the carrying of the current. Discharges of 10 to 20 amperes have been maintained for many hundreds of hours with a tungsten cathode at a temperature of about 3000° K., where the vapor pressure of the metal is 3.6×10^{-4} mm. of Hg. Under these conditions the rate of evaporation does not appear to be any greater than that due to temperature alone, as in a lamp filament.

Dr. Langmuir has shown that in a high vacuum the normal electron emission at 3000° K. is 31.7 amperes per square centimeter of surface. Due to elimination of "space charge" by the production of positive ions, the whole of this current should be obtained in the presence of a conducting gas, and it may further be augmented by secondary electron emission from the cathode produced by positive ion bombardment, and also perhaps by thermionic emission from the gas itself, the temperature of which is undoubtedly very high.

Since tungsten has such a low vapor pressure in comparison with other metal and carbon electrodes, which latter often reach the boiling point under arc conditions, we should expect a marked difference in the electrical characteristics of the arcs. This, however, does not appear to be so.

Chemical reaction at the electrode surface with the formation of more or less volatile products, in the case of the presence of oxygen, nitrogen, chlorine and some compounds, seems to inhibit electron emission rather than to excite it. For instance, if an arc in nitrogen be produced between tungsten electrodes, the arc is quite stable. If, however, oxygen be admitted, a volatile tungsten oxide is rapidly formed at the electrode surfaces, the arc drop is increased, and a much higher voltage is required to maintain the arc.

Irving Langmuir: I think the point that Mr. Cady raises about definitely defining the arc is one we ought to think over very seriously. It seems to me that the old definition of an arc, or in fact any definition which is tied up in any way with the emission of vapor from the electrode, is not a proper one to use at present. Those who have studied arcs in inert gases, particularly with heated tungsten electrodes, such as those described in the paper by Mr. Darrah, will find that vaporization from the electrodes has nothing whatever to do with the phenomenon.

In a recent article by Mr. Meikle (General Electric Review (1916) **19**, 297), arcs in nitrogen and in argon between tungsten electrodes are described. In some cases Mr. Meikle has had currents as high as 80 amperes with relatively low voltages, and the discharges have had all the characteristics of what we commonly call an arc; with two electrodes an inch apart, the discharge looked like an arc, was hot, etc., and yet there was no appreciable consumption of the electrodes. The electrodes do gradually lose weight, but do not lose weight in many cases as fast as if they were heated to the same temperature in a vacuum by other methods. The tungsten vaporizes a little, but so little that you cannot see any tungsten spectrum in the arc. On the other hand, you can use a metal which vaporizes more easily, and can get the vapor in the arc, without essentially changing any of the characteristics. Naturally, if you use electrodes that vaporize, the vapors will get in your arc path and produce a spectrum and may change the electrical characteristics just as any substitution of one gas for another might do, but in many cases they produce no essential change in the arc, except the introduction of a spectrum. It therefore seems extremely unwise to have the definition of an arc in any way connected with the production of vapor from the electrodes.

I would like to hear the opinion of others on this, and I hope Mr. Cady will take up this point in answering the discussion.

Recently there have been published some articles in the Proceedings of the Royal Society, by Duffield and some one else, on the consumption of electrodes in arcs. He deals with carbon arcs, and finally reaches the conclusion that four electrons are emitted for one carbon atom; in other words, Faraday's Law practically applies. This is certainly not the case with tungsten, and it certainly does not apply in the case of carbon in an inert atmosphere. I believe the consumption of carbon takes place simply because it is heated to a temperature at which it vaporizes. It is thus a secondary phenomenon, due to the fact that the carbon gets hot and vaporizes, but which has nothing to do with the arc.

W. R. Mott: I would like to ask Dr. Langmuir if the phenomenon observed by Duffield (Roy. Soc. Proc. (1915) **92**, 122-143), in the carbon arc, can be extended in any way to the tung-

sten arc, since Allgemeine Electricitäts Gesellschaft (Eng. patent (1900) 11660) indicates that tungsten moves from positive to negative in a tungsten arc in inert gas.

IRVING LANGMUIR: All I can say is that tungsten may be carried in either direction by an arc passing between tungsten electrodes in inert gas, and apparently the electrical discharge does tend to carry down the vapor and precipitate it on one electrode more than the other. That is only to be expected. It is expected, if you have tungsten vapor, it will be ionized, as any gas will be, and tend to wander towards one electrode or the other, and therefore the total loss of weight of one electrode may be slightly different from the other, even at the same temperature. It is a secondary phenomenon and not a primary phenomenon.

In the experiments we have made the amount of tungsten vaporized comes out at about 1/10,000 of the Faraday equivalent of tungsten which should be carried from one electrode to the other.

W. G. CADY: Mr. Mackay states that the presence of oxide on the cathode sometimes raises the arc drop instead of lowering it. This may well be, for Wehnelt (Annalen der Physik (1904) **14**, 427) found enormous differences in the case with which different oxides emitted electrons when heated.

As Mr. Langmuir has said, the main point at issue is, what shall be chosen as the definition of the electric arc. Consider what happens in the case of a cathode of low volatility when the current in a glow discharge in an inert gas is gradually increased beyond the limits usually observed in such discharges. The discharge becomes brighter, the end of the positive column advances toward the cathode, and the cathode itself becomes incandescent. Owing to the last effect, the drop in potential at the cathode becomes smaller. This has been known for many years. The early papers of Hittorf and of Lehmann contain descriptions of such discharges, which they recognized as being fundamentally glow discharges. There is, I think, no essential difference between these forms of discharge and those described by Messrs. Mackay, Langmuir, and Darrah. The difference is only one of degree, and the gap might be bridged in a perfectly continuous manner. I do not think that a philologist would warrant giving two dif-

ferent names to the same type of discharge. On account of its low volatility, tungsten is almost unique in its unwillingness to arc when used as a cathode in an inert gas. Under these conditions the discharge may well present all the external characteristics of an arc, except the disintegration of the cathode.

There is also a strong historical reason for adhering to the stipulation that the material from the cathode must appear in the discharge if the latter is to be called an arc. The first arc was so called because Sir Humphrey Davy observed an arc or bow of light between charcoal electrodes when he first obtained the discharge by means of a battery of 2,000 primary cells, in 1808, and the name has stuck ever since. Through all the literature down to the most recent times it has been assumed that the phenomenon involved vaporization of the cathodes. This feature of the discharge has been of no less interest to the spectroscopist than to the illuminating engineer. It is characteristic of the usual, normal gas discharge at high-current density. I do not think that the importance of the discharge from a hot non-vaporizing cathode is well enough established as yet to warrant straining a point in order to let it be covered by the term "arc." I believe that in general, even in this form of discharge, it will be found possible to increase the current to a point where local vaporization of the cathode suddenly sets in, accompanied by a constriction of the discharge and an abrupt diminution in the fall of potential at the cathode. This stage is the true arc.

Irving Langmuir: I take a different stand from Mr. Cady. It seems to me as the evidence stands at present that the things that have been called arcs are not dependent essentially upon the presence of vapor from the electrodes. The old form of arc is one between two carbon electrodes in the air. As I understand the mechanism at present, the vaporization of carbon from the electrodes is only a secondary phenomenon. If you put a carbon arc in argon or in nitrogen, or in any other gas, the loss of weight of the electrodes will be different for each gas, or, if you draw the arc out and make it sufficiently long so that the vapor of the electrodes does not go into the center of the arc, the phenomena are not very radically changed, but the loss in weight is very different. I would like to propose that we define an arc as a con-

tinuous discharge in which the current through the gas is rather localized along a distinct line between the electrodes.

It seems to me the development of that idea would lead us to something which would be more useful and yet consistent with all the old definitions of arcs, and would include all these newer forms of arcs we are getting with non-consuming electrodes, and would exclude the glow discharges, even though the glow discharges may be obtained from the arc by continuous steps. That is not a reason which should keep us from having different names. We distinguish between a liquid and gas, notwithstanding the fact that we can pass from one to the other by continuous changes. We can have arcs, and glow discharges then, even if we cannot sharply define them under certain conditions.

W. G. Cady: It is not fair to the other speakers to prolong the discussion. I wish that a committee of this Society or a joint committee of several societies might some time be appointed to formulate a proper definition of the electric arc.

Taking as the criterion for the arc the localization of the discharge along a narrow path, I would remind you that in any gas at rather high pressure the glow discharge is localized along a line down the center of the tube whether the electrodes are hot or cold. In order to define anything, a statement must be definite; bearing this in mind, the only satisfactory definition that I know of for the electric arc is one that involves the vaporization of the cathode at the base of the discharge.

A paper read before the New York Section of the American Electrochemical Society, in Joint Session with the Illuminating Engineering Society, on November 11, 1915. Called up for Discussion at the Twenty-ninth General Meeting of the Society, in Washington, D. C., April 27-29, 1916.

THE ELECTRIC ARC IN VAPORS AND GASES AT REDUCED PRESSURES.

By W. A. Darrah.*

Present commercial arc lamps operate with few exceptions in an atmosphere rich in oxygen or the oxide compounds of the electrodes. As a result the electrodes are oxidized as rapidly as they are vaporized (if not already composed of oxides, as in the case of a magnetite arc), and as the oxides cannot be used again commercially it is necessary to provide means for disposing of them. This cycle of vaporization and oxidation of the electrodes naturally results in their comparatively rapid consumption, which necessitates the trimming and cleaning of the arc lamp, one of the large factors of arc lamp operation.

If it were possible to so design the lamp that the supply of material for the arc did not come from the electrodes but from a surrounding gas or vapor, and if in passing through the arc the vapor were not destroyed it would then seem to be possible to construct an arc lamp which would not require trimming or materially more attention than an incandescent lamp. A lamp of this type, if it had a white light and good efficiency, might in some cases even occupy the field of the present incandescent lamp.

The research which is described in this paper was carried on to investigate the possibilities of accomplishing this object and, while the results are very promising from a practical standpoint, they are outlined here for their scientific value and should be considered only as a scientific research.

A study of the light efficiency of an arc from a chemical standpoint shows that there is a certain rather limited class of substances which when introduced into the arc in small quantities produce a very great increase in luminosity. Thus the addition of small quantities of cerium or calcium compounds to the car-

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bon arc may increase its efficiency over 300 percent and the addition of titanium (preferably as an oxide) to the magnetite arc similarly produces an increased luminosity without a corresponding increase in energy consumption.

It is a peculiar coincidence that the addition of cerium or calcium to the magnetite arc, or titanium to the carbon arc does not result in approximately the same gain in efficiency. The chemical compounds in which the element appears is apparently of little importance.

A study of these facts led to the conception that perhaps an arc could be maintained in a closed vessel and supplied with these light-producing elements in the vapor form. On investigation this did not seem impractical, especially after a consideration of the liquid "inorganic" compounds shown in Table I, which contains some of the elements which produce highly luminous arcs. The table is discussed at length later on in this paper, but it is interesting to note that titanium, tungsten and other elements which increase the luminous efficiency of an arc, may readily be secured in the form of volatile liquids.

Accordingly, a crude apparatus was arranged in which two hard-carbon electrodes were placed vertically above each other in a tight glass vessel, and an arc drawn between the electrodes. As might be expected, this arc was non-luminous and very unstable. Accordingly, a small amount of carbon tetra-chloride was poured into the vessel with a rather marked result. The arc then became stable and could be drawn out to several times the length which was previously possible, although its luminosity was not much increased. A flaky soot formed by the decomposition of the carbon tetra-chloride also filled the glass chamber. A trial was next made with stannic chloride with a similar increase both in stability and allowable arc length. In this case also the luminosity of the arc was much greater. The stannic chloride, however, was decomposed by the air and moisture present, forming a white insoluble powder upon the walls of the chamber, soon shutting out most of the light.

A more elaborate apparatus was therefore constructed in which the graphite electrodes were separated by an electro-magnet acting upon an iron core within a glass chamber. (See Figs. 1 and 2.)

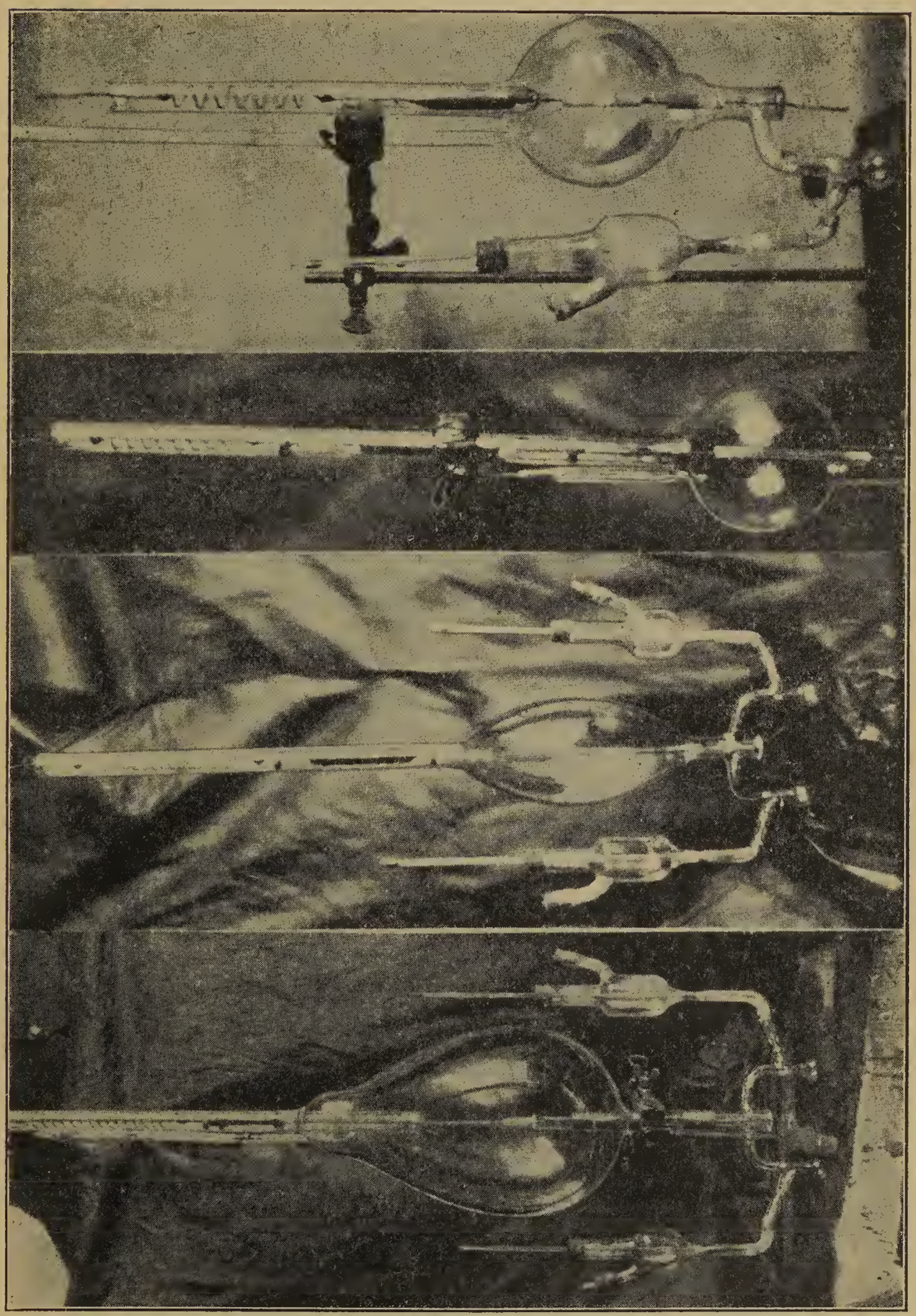

FIG. 1. FIG. 2. FIG. 3. FIG. 4.

The air was exhausted from the chamber, a small quantity of stannic chloride vapor at a pressure of from 3 to 4 cm. of mercury was allowed to enter and the arc drawn. Under these conditions a stable arc 3 to 4 inches (7.5-10 cm.) long could be produced with 6 to 7 amperes direct current, and 220 volts impressed. The arc was intensely white and so steady that it had the appearance of a thick incandescent filament slightly bowed and surrounded by a flame-like less luminous shell of yellow. The vapors from this arc, however, soon collected on the walls forming a dense brown coat which proved to be mainly tin carbide, with a mixture of stannous chloride and other intermediate compounds. A photograph of this lamp, which was used entirely on direct current, is shown in Fig. 1.

These preliminary tests having indicated possibilities as well as having shown the difficulties to be overcome, additional smaller lamps were constructed along the lines shown in Figs. 3 and 4. With these a detailed study was made of the effects of the various available electrode materials as well as the different vapors and lamp designs.

For convenience a hard glass (manufacturer's number G-702-P) was employed, as this permitted the sealing of tungsten wires and rods directly into the globe by the use of a flux of potassium nitrite and borax. This allowed the free use of heavy seals which were necessary for the tests. The shapes shown in Figs. 2 and 3 were found fairly satisfactory, while Fig. 5 shows some later designs which eliminated many of the difficulties eventually encountered.

The type of lamp shown consists essentially of an arc chamber at the center of which the arc is drawn between two tungsten electrodes about $\frac{3}{16}$ inch (0.5 cm.) in diameter. The electrodes are partly surrounded with a refractory insulator designed to prevent the arc from moving far from the ends of the electrodes, as this allows the magnetic blow of the arc to continue to extend it, ultimately tending to rupture the arc. The refractory insulator also assists in maintaining the electrodes at a high temperature, thus increasing the efficiency of the lamp and the stability of the arc.

The upper electrode is fastened by means of a tungsten rod to an iron core which is surrounded by a glass shell to protect

the iron from corrosion as the vapors used readily attack nearly all metals except tungsten, platinum, gold and a few other inert materials. A flexible tungsten spiral serves to conduct the current from the upper movable electrode to the upper seal.

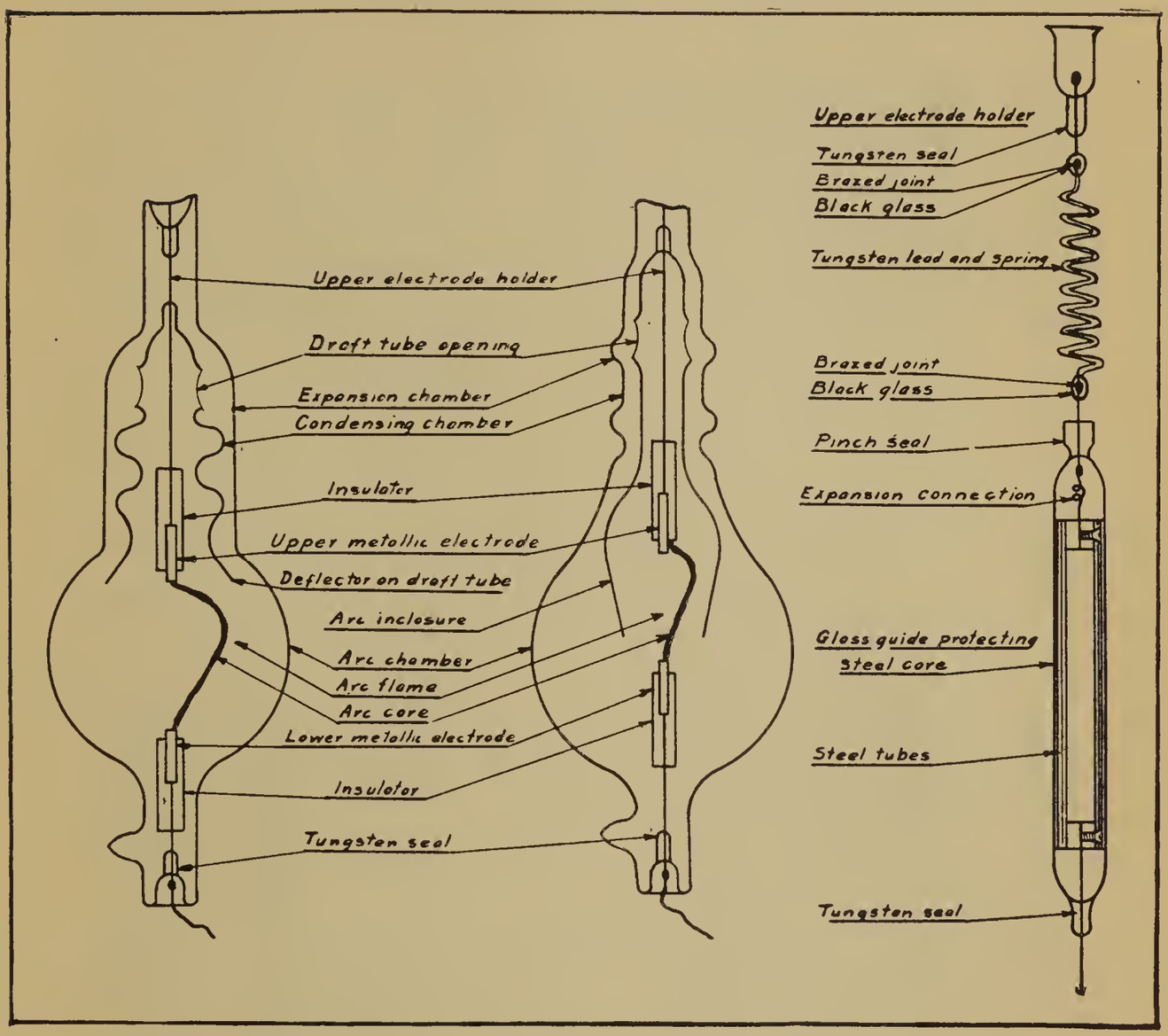

FIG. 5.

It was found after a number of trials that a certain combination of gases to be described later gave a minimum amount of "soot" (decomposition products), which gradually collected upon the globe, thus reducing the amount of light radiated. In order to overcome this difficulty the arc chamber was extended somewhat above the upper electrode, thus forming a condensing chamber in which the soot could collect, allowing the walls to remain clean.

Further study developed that while this would remove a large quantity of the suspended soot a certain amount was still deposited on the glass walls adjacent to the arc. In order to eliminate this deposit, a draft tube was placed around the upper electrode in such a position that the heated gases from the arc would pass upward through the draft tube out into the condensing chamber and then back downward into the arc chamber for use again. The corrugations shown on the draft tube and condensing chamber have the effect of slightly compressing and expanding the gas as it passes from a chamber of small volume to one of large volume. The alternate expansion and compression of the gases, as well as the contact with the walls thus produced, was found to materially aid the condensation of the suspended matter.

TABLE I—EFFECT OF VAPOR ARC.

Substance	Boiling Point C°	Melting Point	Effect on Arc	Luminosity	Color
1. Carbon tetra-chloride .	77°	Liquid at ordinary temperature	Stable	Low	White
2. Stannic chloride	114°	Do.	Stable	Medium	Yellow white
3. Titanium tetra-chloride	136°	Do.	Unstable Oscillatory Arc	Very high	White
4. Antimony trichloride ..	220°	Do.	Stable	High	Yellow white
5. Arsenic chloride	130°	Do.	Stable	Low	Purple
6. Silicon tetra-chloride .	57°	Do.	Unstable	High	White
7. Boron chloride	18°	Do.	Unstable	High	White
8. Phosphor trichloride ..	75°	Do.	Stable	Low	Pink and green
9. Aluminum trichloride .	183°	Volatile	Do.	Low	Yellow
10. Cerium chloride	1400°	.....	Do.	Very high	White
11. Calcium chloride	1200°	780°	Do.	High	Strong yellow
12. Calcium iodide	1100°	740°	Do.	High	Yellow
13. Chromic chloride	White heat	.....	Unstable	Low	Green
14. Titanium chloro bromide	180°	.....	Very stable	Very high	White
15. Bromine	63°	7°	Very stable	Low (high absorption)	Yellow
16. Iodine	114°	Volatile	Unstable	Low	Blue
17. Chlorine	33°	102°	Stable	High	Yellow

The search for a satisfactory electrode material developed that carbon, whether in the form of graphite or in the amorphous state, was unsatisfactory because of the disintegration by the action of the vapors and also the deposit of free carbon which it caused on the walls of the arc chamber apparently by direct radiation, as

the draft tube and condensing chamber did not affect it as much as an increase of pressure of the gas around the arc.

It was demonstrated that practically all of the materials available (see Table I) formed carbides under the influence of the arc, and these carbides mixed with free carbon formed so heavy a deposit on the walls of the arc chamber that it was decided to abandon carbon.

Chromium, titanium, molybdenum, nickel, iron and silver were all tried without satisfactory results. Decomposition of the electrodes, decomposition of the surrounding gases and heavy deposits on the globe made the use of these materials impractical.

The substance which was found to be satisfactory in all respects was tungsten, which proved to be practically inert even at a white heat in the presence of the various vapors used. The tungsten terminals moreover did not melt or evaporate in the arc except at a very slow rate which seemed to be comparable to the evaporation of the filament in an incandescent lamp. A rather interesting phenomenon resulting from the gradual evaporation and deposition of the tungsten electrode was exhibited in the growth of a thin star-shaped fringe on the edges of the arc surfaces of the electrodes. This fringe was composed of points two or three millimeters long formed of small needle-like crystals of tungsten, and appears to be caused by the slow precipitation of free tungsten from the surrounding gases under the influence of temperature changes.

Having devised a satisfactory construction it was found that in order to introduce the gases and eliminate air and moisture, special methods were required.

As all of the liquids employed are hygroscopic and many of them readily decomposed by ordinary moist air, it became necessary to exhaust the air from the lamp, heat the lamp and electrodes while at a low pressure, in order to remove the air films, and then admit the liquids without opening the lamp chamber to the air. This was accomplished by means of a bottle sealed to the lower extremity of the lamp and provided with a ground stop-cock connecting it with the lamp as shown in the photographs. After the proper degree of exhaustion was reached, the desired liquid was carefully poured into the bottles and the stop-

cock opened slightly, when atmospheric pressure forces the liquid into the lamp chamber.

The appearance of the arc in this lamp is quite different from other commercial arc lamps (see Figs. 6 and 7). It is usually very stable, about ⅛ inch (0.3 cm.) in diameter, tubular in form and varies from 2 to 5 inches (5-12.5 cm.) in length with 110

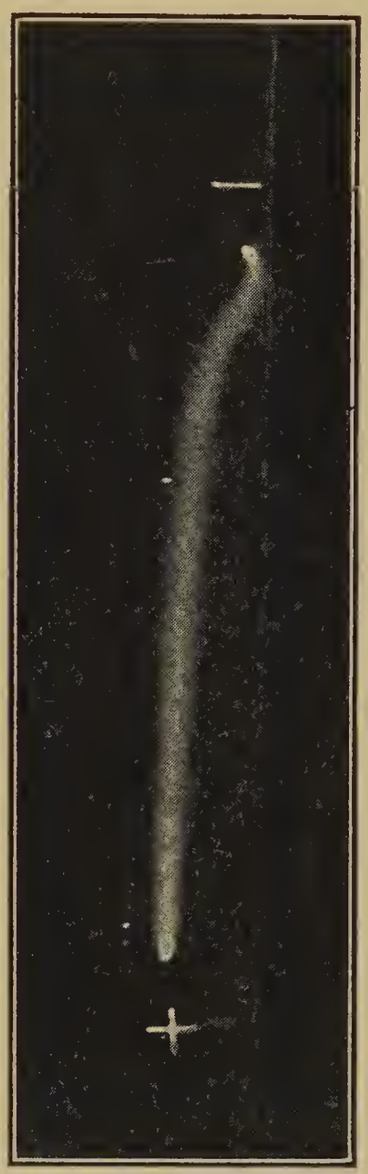

Fig. 6.

Fig. 7.

volts direct current applied, the variations being due to differences in pressure, nature of the gases supplied, etc. A high pressure naturally increases the intrinsic brilliancy of the arc but makes it necessary to operate at a shorter length, as the gas currents due to temperature differences and arc reaction are correspondingly more violent. The diameter of the central luminous tube is also reduced with an increase in pressure.

Some of the arcs revolve very slowly, but as a rule the low pressure of the gases minimizes the motion of the arc and the general appearance is that of a thick intensely white incandescent filament slightly bent at the upper end. With some of the vapors, as for example the metalloid halogen compounds, antimony, phos-

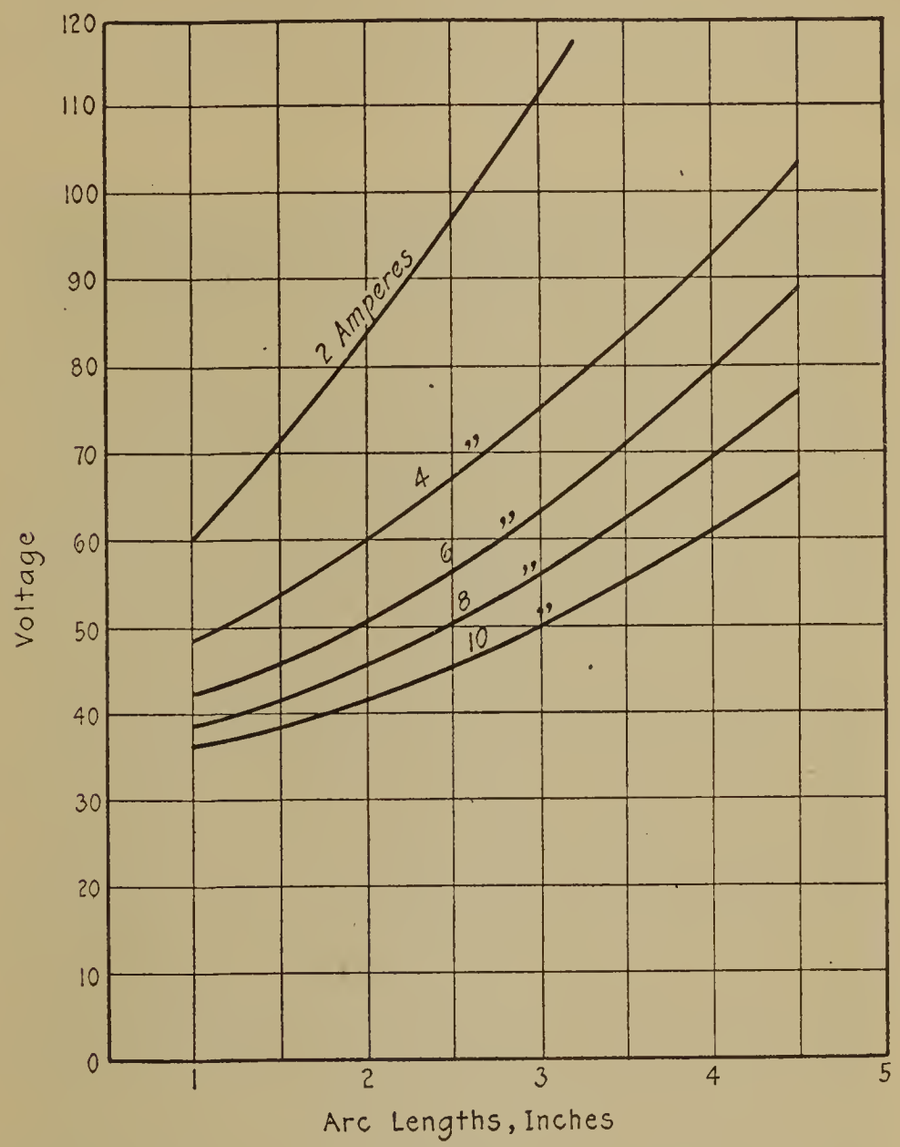

FIG. 8.

phorus and arsenic chlorides, the central tubular portion is surrounded by a ragged flame which is light pink in the case of arsenic and pale green in the case of phosphorus.

The flame portion acts somewhat as an absorbing screen, thus reducing the total useful radiation. It is a curious fact that this flame may exist for a short but appreciable time after the circuit has been interrupted, thus indicating that it probably does not have a part in the conduction of electricity through the vapor

but appears to be a zone in which the vapors, after being dissociated by the heat and electrical effects of the arc, recombine. The spectrum of the flame is usually quite different from the arc spectrum and is characteristic of the elements involved, while the spectrum of the arc independent of the ends of the electrodes (which of course give a hot-body spectrum), is usually a band spectrum and is practically continuous except for a few absorption lines.

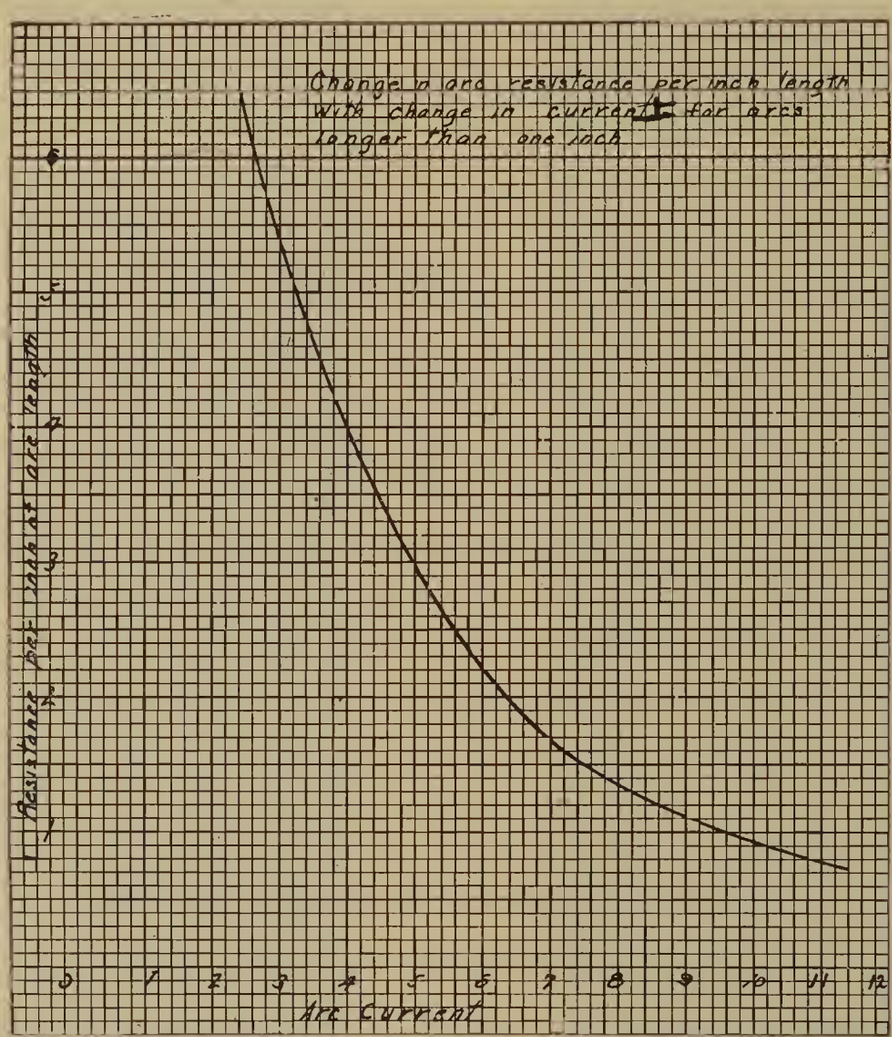

Fig. 9.

A curious phenomenon noticed with an 8 ampere 220 volt arc at low pressure in the presence of cerium chloride was a separated arc which gathered into a glowing sphere at one corner of the chamber, while the space between the electrodes through which a current of eight amperes passed was entirely dark.

Figs. 8, 9 and 10 are typical performance curves and indicate the electrical characteristics of the antimony pentachloride lamp,

which is illustrative but does not have as high an efficiency as the titanium tetra-chloride or titanium bromo-chloride lamp.

Fig. 8, plotted between arc length and voltage, shows the rate at which additional arc lengths require an increased voltage. The curve is also interesting as indicating that a 4-inch (10 cm.) arc at 10 amperes requires no more voltage than a 1-inch (2.5 cm.) arc at 2 amperes. In other words a 10-ampere arc is four times as long and therefore emits four times as much light as a 2-ampere arc. In addition its intrinsic brilliancy is about five times that of a 2-ampere arc. Accordingly, the light emitted by a 10-ampere arc *under these conditions* is twenty times that of a 2-ampere arc, and since the wattage of a 10-ampere arc is only about five times that of the 2-ampere arc, the efficiency is approximately four times that of the 2-ampere arc.

Efficiency curves indicate that 20 amperes is approximately the point of maximum efficiency of this particular antimony pentachloride lamp. It should be understood, however, that the current of maximum efficiency differs widely with differences in the nature and pressure of the gas as well as the volume and available radiating surface of the lamp, and very efficient titanium bromo-chloride lamps have been constructed with a maximum efficiency of about 5 amperes.

Fig. 9 shows the change in arcing distance for unit arc length with a given change in current, and indicates (if continued) by the rapid initial rate of decrease in resistance that maximum efficiency is reached at about 20 amperes. This curve also gives a basis for comparing the electrical stability of the low pressure arc with that of present commercial arcs.

Fig. 10 shows the decrease of voltage at the arc with increase of current and gives further data on the stability of the arc and the amount of sustaining resistance necessary. It will be noted also that the dotted curves showing the true arc voltage tend to converge to a point of minimum arc voltage at about 20 amperes, thus again indicating that the particular vapor in question (antimony pentachloride) will give most efficient results at about 20 amperes.

Regarding the power consumption, it is to be expected that this will vary widely with the condition and nature of the vapors used, and actual results range from 1 watt per mean spherical

candle power to less than one-quarter of this value. This performance may be secured with a white light which closely resembles afternoon daylight (north sky). An analysis of the color of the arc with the spectroscope as well as color matching tests, confirm this fact.

As a matter of interest, Table I shows some of the different

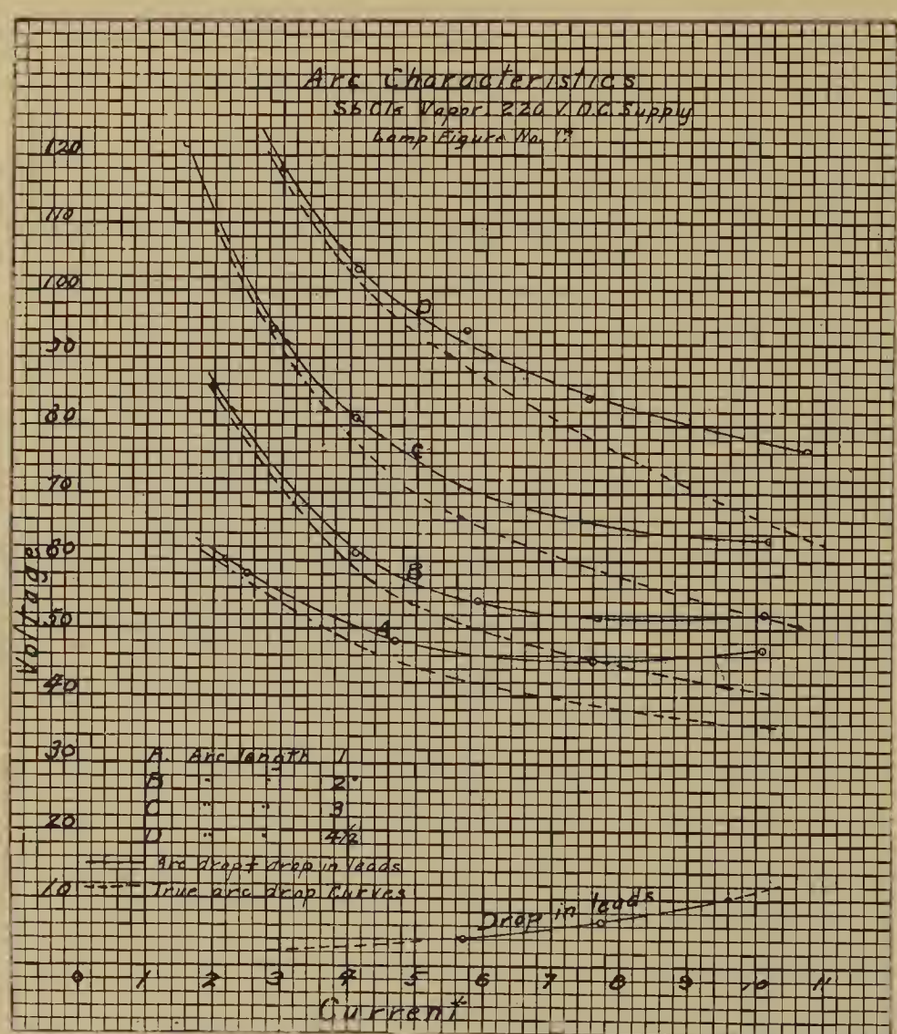

Fig. 10.

compounds tested and some of the general results secured. These compounds may be roughly divided into three classes, as follows:

(A) The illuminants or those materials which give a high luminous efficiency. They usually produce unstable arcs if used alone.

(B) The stabilizers or those compounds which have a low luminous efficiency but when introduced into an arc allow a very stable arc at relatively low voltages.

(C) The "catalyzers," or those compounds which are intro-

duced to assist recombination in the flame zone, thus minimizing deposit.

Table I is interesting, as it is the peculiar properties of the compounds, many of which are not very commonly used, that render possible a lamp of the kind described. The problem is to introduce as dense as possible an atmosphere of the various illuminants, as titanium tetra-chloride, into an arc in such a form that it will not be permanently decomposed but may be used again and again. Some of the liquid halogen compounds shown in the table allow this. Some of these compounds (as for example those with the metalloids) which have a relatively slight affinity for a halogen, are too readily decomposed to be useful. Others, like stannic chloride, are too readily reduced to a less oxidized state, passing from a tetra-chloride to the di-chloride. Titanium tetra-chloride is an example of this condition, but the addition of a small quantity of free bromide to the $Ti\ Cl_4$ (in which it is readily soluble) forms a compound which readily recombines after dissociation.

Fortunately also, since the chloride and bromo-chloride of titanium dissociate at a higher temperature than tungsten chloride, and therefore recombine at a higher temperature than tungsten chloride, these vapors will not attack metallic tungsten even in the presence of the electric arc.

In order to avoid oxidation effects it was necessary to eliminate all oxides from Table I. More complex compounds such as sulphates, nitrates, could not be considered because of the tendency to dissociate and not recombine. Sulphides, nitrides, phosphides, etc., were eliminated because the chemical stability of these compounds in most cases was too slight to be satisfactory.

Chlorine was the halogen most generally used, because of the stronger union of the chloride, and the reduced tendency of the dissociation products to attack the tungsten electrodes.

A sketch of the finished lamp is shown in Fig. 11. This illustrates schematically the containing glass vessel hermetically sealed, the current being carried into the lamp by heavy tungsten wires. The upper electrode is carried on a floating iron core and a magnet coil around the outside of the tube, but in series with the arc, serves to lift the upper electrode automatically to the desired separation and hold it suspended under such conditions that the

separation immediately compensates for changes in current value. By the proper dimensions and design of coil and core, stable operation may be secured without the use of a dash-pot.

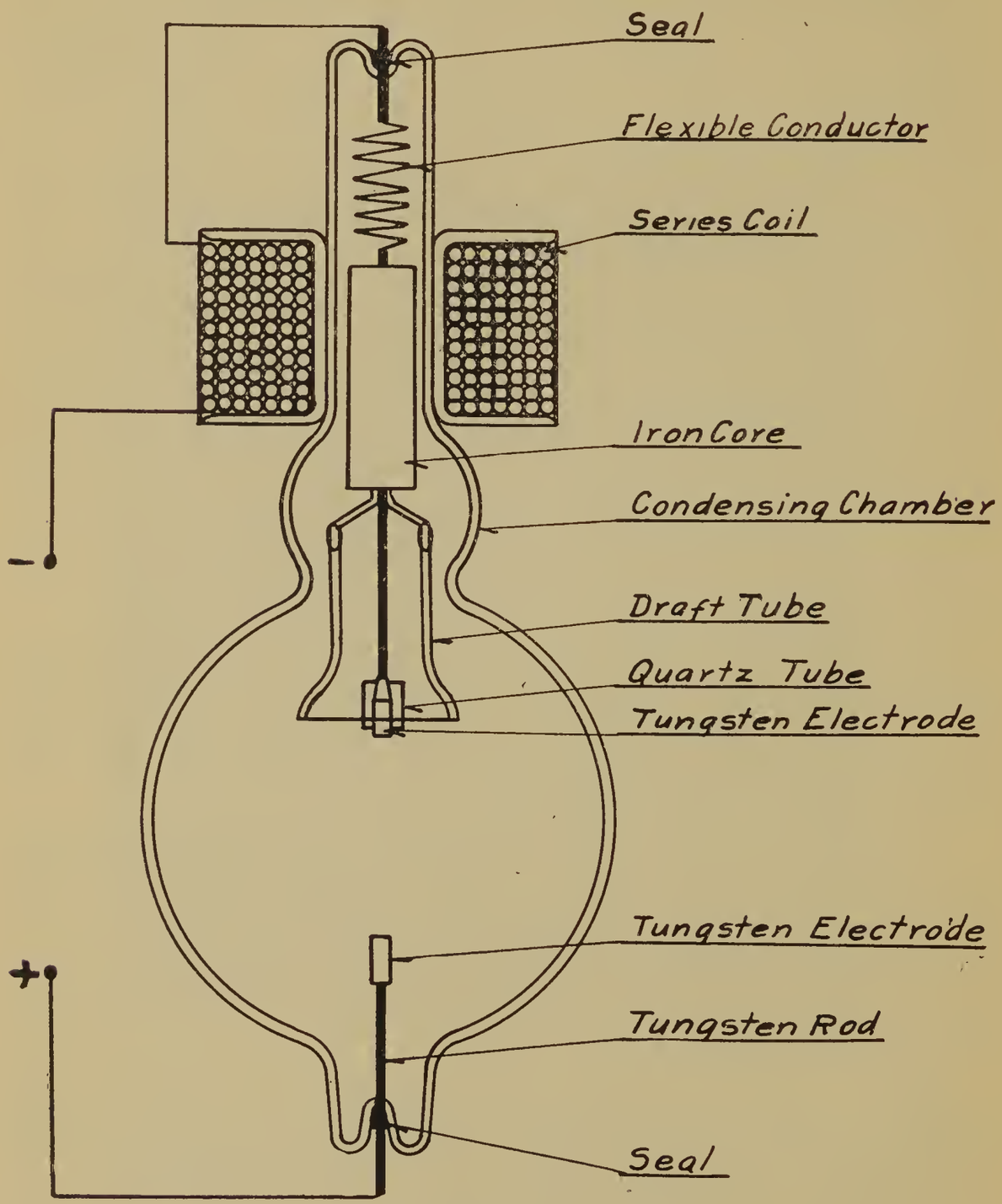

Fig. 11.

To start the lamp it is only necessary to apply current to the terminal. When the circuit is completed the current passes through the electrodes (which are held in contact by gravity), then through the flexible lead to the series coil which it energizes, causing the magnet to separate the electrodes, thus drawing the

arc. The arc immediately becomes extremely brilliant although there is a slight increase in efficiency for ten to fifteen minutes, after which the lamp reaches operating temperature and conditions become stable.

Satisfactory stability is dependent upon proper temperature and pressure conditions. A pressure within the cold lamp of from 2 mm. to 15 mm. of mercury was found workable with the gases used. About 6 mm. pressure was a very satisfactory condition.

The bulb of the lamp for operation on about 8 amperes, 110 volts, is 4½ inches (11 cm.) in diameter. This spacing allowed the heat from the arc to maintain the walls at about 220° C., which gives a stable arc with titanium bromo-chloride and allows the globe to remain clean and the life long. As this temperature (at the pressures within the lamp) is above the boiling point of the titanium bromo-chloride, no condensation can occur.

The life of a lamp constructed as here described is limited by the consumption of the gases and the evaporation of the electrodes. As a result of actual test, the consumption of the gases is extremely slow, due to the fact that only a small portion is not recombined after passing through the arc. The evaporation of the electrodes of course depends upon the rate at which heat is supplied the electrode, the rate at which heat is radiated from them, the pressure within the lamp, and the nature of the gases. In a ten-ampere lamp operated for about 950 hours, the total length of electrode consumed was about ⅛ inch (0.3 cm.), or a volume of about 0.00155 cubic inches (0.025 c.c.).

There is also a slight but progressive darkening of the globe which becomes appreciable at about 1,000 hours. Further developments are in progress for reducing this factor, which appears at present to be the feature that limits the life of the lamp, although in its present stage it appears that 1,000 hours is a conservative estimate.

When properly adjusted and operated at the correct temperature and pressure, the lamp appears to very largely eliminate the difficulties such as the welding of electrodes, the formation of an insulating slag upon the ends of the electrodes, and other similar difficulties which are responsible for a large portion of the outage in present types of arc lamps.

It would appear that an investigation along the lines here described opens up new possibilities in light production, but it cannot be too strongly emphasized that while the results set forth in this paper offer considerable promise from an applied, practical standpoint, yet they are not presented for consideration as representing a finished device but merely a research in what seems to be a new and interesting field.

Mansfield, Ohio.
Nov. 1, 1915.

DISCUSSION.

(*In New York City, November 11, 1915.*)

G. M. J. Mackay: In working along somewhat similar lines to Mr. Darrah, we found the following phenomenon occurring when tungsten electrodes were used in an arc with halide gases. The cathode at its hottest point, at the spot from which the arc apparently started, was practically unattacked by the gases. At a cooler portion of the electrode, however, the tungsten was slowly eaten away, so that finally the cathode proper would remain attached to the lead by merely a thin neck. This seemed to indicate that at the temperature of the cathode spot, any compound possible between the halogen and tungsten would be dissociated, so that no permanent combination could occur, but that at a more or less definite lower temperature, the halogen, dissociated by the heat of the arc, would combine with the tungsten to form a compound stable under these conditions. In this case the chemical reaction occurring would seem to be merely a secondary effect of the arc, and in no way connected with the conduction of current.

I should like to ask Mr. Darrah if he has had a similar experience.

W. R. Mott: I take exception to Mr. Darrah's statement that "The chemical compound in which the element appears is apparently of little importance." From my experiments, I believe

that the chemical compound is often of the greatest importance and in the case of calcium fluoride the arc spectrum is that of metallic calcium lines plus the bands due especially to calcium fluoride and given by no other element or compound. From a spectroscopic standpoint, the fact stands out that calcium fluoride owes most of its beautiful, intense light to other factors than the elemental line spectrum. The contrast between CaF_2 in carbon arc *versus* magnetite arc and of TiO_2 in similar conditions may be explained by the difference in the chemical relations.

Dr. Monasch (The Illuminating Engineer (London) April, 1910, p. 253) has given horizontal candle power of magnetite electrodes containing added materials at 80 arc volts and 4 amperes. I quote a few of the results.

Substance	Formula	H. K.
Calcium Fluoride	CaF_2	1940
Titanium Oxide	TiO_2	1370
Tungsten Oxide	WO_3	700
Titanium Metal	Ti	549
Tungstic Dioxide	WO_2	400
Magnetite	Fe_3O_4	300
Iron Metal	Fe	99 to 141
Calcium Oxide	CaO	60
Copper Metal	Cu	25

The calcium fluoride gave in the absence of carbon about thirty times as much light as calcium oxide. The metals were less efficient than the compounds. The oxides of metals having two or more valences generally gave the higher candle power. Also, of two such oxides, the one of higher valence generally gave the more light. Even calcium fluoride in a flame arc could form temporarily a sub-fluoride.

Dr. Langmuir's experiments and Mr. Darrah's results bring us to the conclusion that tungsten represents probably the least volatile of known elements. Hence the incandescent-filament lamp manufacturers are extremely unlikely to make any superlatively great advance in efficiency such as can be made in the flame arc. Mr. Darrah has shown us a new way in which very high efficiency and high quality of light can be obtained.

Finally, I wish to congratulate Mr. Darrah on his making a notable contribution to the science of illumination of the flame arc.

W. C. Moore (*Communicated*): Mr. Darrah's work is an important entering wedge into a field which with proper cultivation should give us a commercial type of lamp.

In the first place, as a carbon chemist, my attention is naturally directed to the failure of a carbon electrode for this particular class of work. As is well known, different varieties of arc carbons show different properties under the same conditions, and in this connection I should like to ask Mr. Darrah if he has tried several varieties of amorphous arc carbons under reduced pressure, and, if he has, whether he has any information as to their source and history. Several months ago I noticed a very rapid darkening of a capillary tube, in which a spark was passed between flame carbon electrodes in an atmosphere of nitrogen. Admission of air to the tube while sparking removed this dark deposit. This deposit was not examined but might have been para-cyanogen; so that under certain circumstances a blackening like that mentioned by Mr. Darrah can occur very rapidly at ordinary pressure.

The work of Pring and Fairlie (Trans. 8th Inter. Cong. Applied Chem. (1912) **21**, 65) shows that amorphous carbon is increasingly more reactive toward hydrogen above 1,000° C. than is graphite when methane is formed. Moreover, the work of Schenck and Heller (Ber. (1905) **38**, 2139) indicates that the vapor pressures of so-called amorphous varieties of carbon are greater than that of graphite at temperatures near 600° C.; and in view of what Mr. Darrah says about the evaporation of carbon from his electrodes, it would be interesting to know if he has observed any great difference not only in the reactions of these several varieties of carbon and of graphite with the gases in his lamp, but also in the rates of evaporation of the different carbon materials.

Coming now on another point, those of us who are most interested in the flaming arc find it rather difficult to explain all the phenomena observed in such an arc in terms of the electron theory. It may be that, as chemists, we are not as familiar as we might be with all the details of this theory; in fact, it seems to some of us as if each worker in this field has his own electron theory. It is well known, however, that this theory gives us an insight into many of the phenomena of gaseous conduction, and

I would like to know what success Mr. Darrah has had in applying this theory to this work?

The recent work of C. D. Child on the mercury arc is of interest in this same connection (Phys. Rev. (1914) **4**, 389). It will be recalled that Child has advanced the idea that in the mercury arc the positive ions Hg^{+} and Hg^{++} play an important part in the production of light; the union of Hg^{+} with an electron giving rise to the yellowish light, the union of H^{++} with two electrons giving the green light. The work of Bancroft (J. Phys. Chem. (1914) gives support to the view that Hg^{+} combining with one electron gives orange light. In view of these researches, one is led to wonder if, after all, positive ions which are identical with ions formed in solutions are not sometimes partly responsible for light production in the arc.

The successful use of tungsten as an electrode material may throw some light on the temperature of this arc.

Since Langmuir's (Phys. Review (1915) **6**, 138) recent results show that tungsten melts at 3540° K., this arc under these low pressures must have a lower temperature than the melting point of tungsten. However, we do not know much about the relative temperatures of the arc and the electrode ends. We do know that decrease of pressure lowers the arc temperature. A common statement in text-books, patent literature, etc., is to the effect that the flame arc, in contradistinction to the magnetic arc, is a high temperature carbon arc, with the flaming materials "evaporated" into it. A study of the flame arc, especially between solid, impregnated electrodes, would indicate that its temperature is much lower than that of a pure carbon arc. This conclusion is reached on the basis of the relative ease of evaporation of the flaming constituents from commercial carbons, and an approximate idea of the boiling points of some of these flaming materials, for some of which we are indebted to Mr. Mott. For instance, although no highly accurate measurements have as yet been made of this constant, we have circumstantial evidence that the boiling point of calcium fluoride at ordinary atmospheric pressure is a little below 2000° C.

This type of arc increases the number of materials which we have at our command for the production of light. Such elements as arsenic and antimony, and several others with their compounds,

are intensely poisonous and could not be used in flame arc work even if there were no other objections. Moreover, these elements and their compounds, also silicon, germanium, tin, bismuth and lead, have relatively few lines in their arc spectra, and these few lines are for the most part in the ultra-violet region. Mr. Darrah's work, however, shows that in the present instance we are not dealing with the arc spectra characteristic of the different metals used, since the flame he mentions shows the characteristic metal spectrum while the arc proper shows a banded spectrum. The source of this banded spectrum would seem to be a puzzle for the physicists to solve. It might be pertinent to inquire how these bands differ with the different gases? King's work (Astrophysical Journal (1911) **34**) shows that *increase* of pressure in the electric furnace broadens and shifts certain iron spectral lines, while Nutting (Bull. Bureau Standards (1904) **1**, No. 1) has stated that "so far as observations go, acid-forming elements have multiple spectra, while metallic elements do not." Most of the substances studied by Mr. Darrah are acid-formers, and so it is quite probable that we are dealing here with primary spectra. In this type of spectrum, however, there is quite often a *current density* effect; the higher the current density, the greater is the tendency to pass over into secondary or line spectra. Moreover, capacity in the circuit is favorable to the production of secondary spectra, while inductance is favorable to the production of primary spectra. The critical capacity necessary to change over from primary to secondary spectra is dependent on the pressure. the wave length, and the nature of the gas. Decrease of pressure increases the critical capacity, and it is higher toward the blue end of the spectrum.

The considerations seem to point here to Mr. Darrah's having obtained certain of the conditions necessary for maintaining primary spectra; these conditions being low pressure and gaseous materials, all of whose constituents have acid-forming characteristics.

In conclusion, I would say that I feel that Mr. Darrah has made an important contribution to illuminating science in presenting this paper at this time.

W. G. Cady: This is a very beautiful piece of work of Mr. Darrah's, and one in which I am greatly interested.

May I ask what the insulating material was that formed a sleeve close to the tungsten electrodes, and whether it showed signs of being attacked when the arc blew against it, as seems to have happened occasionally?

W. A. DARRAH: I did not measure the drop of potential immediately at the surface of the electrodes, as there did not seem to be enough to be gained by such measurement to warrant the preparation of the necessary apparatus.

My observations on consumption of the electrodes indicated that the upper electrode was always the most rapidly consumed. There was no perceptible difference between the rate of disintegration of the positive and negative electrodes. The rate of consumption was very slow normally, but if air was allowed to enter the chamber or if an excessive amount of free halogen was introduced, then the consumption of the electrodes was rapid and the positive appeared to be affected somewhat more than the negative.

The insulating material used on the electrodes was a small quartz sleeve, placed sufficiently far from the arc not to be vaporized. Under these conditions the quartz did not affect the arc or the chamber of the lamp, but in a few cases in which the arc accidentally came into contact with the quartz, I found it to be readily vaporized. In these cases the silica formed a fine white deposit on the walls of the arc chamber.

Regarding the subject of the necessity for vaporization of one of the electrodes to sustain the arc, I can add no accurate data, but my observations especially from these experiments led me to believe that there is undoubtedly a slight and continual vaporization. I feel, however, that the quantity of material which must be vaporized to produce the necessary ionization to sustain the arc has been generally much over-estimated. In other words, I think that the necessary amount of electrode material to sustain the arc, say for 1000 hours, would from a purely ionic standpoint have a negligible effect on the consumption of the electrodes. By negligible, I of course mean from a practical or commercial standpoint, in connection with the design of a vacuum type of arc.

Regarding the part which chemical reaction plays in the arc, I am inclined to agree with Dr. Moore that this is quite impor-

tant. It will be noted that I pointed out that the flame which surrounds the arc is the seat of rather intense chemical actions, which would seem to be in the case of my type of lamp a recombination of the materials dissociated in the arc. One of the facts to support this belief is the formation of a black deposit, which is frequently either a pure metal or one of the reduction compounds of the metal condensed on a cold body which is placed in the flame surrounding the arc. For example, in the case of a stannic chloride arc I have secured a black deposit which is mainly finely divided tin and stannous chloride, by inserting a cold quartz tube in the arc. In connection with this chemical reaction I have noticed a very peculiar consumption of the electrodes (in those cases where an excess of chlorine or suitable oxidizing agent was present), at points which are not at the maximum temperature. In other words, it would seem that the portion of the electrodes which is brightly incandescent is not attacked by chlorine, but that parts of the electrodes which are less strongly heated may be occasionally attacked.

A very large variety of carbon electrodes were tried, and various forms of hard coke, graphite, and electrode carbon were used. Graphite failed, largely because it seemed to be dissolved by many of the gases which were used. Graphite also caused the formation of carbides, which had the effect of making the globes opaque. Samples of carbon were secured from all of the large carbon manufacturers, but none was as successful as tungsten, which seemed to answer so admirably that carbon was abandoned. I have no accurate data regarding the exact rate of the deposit which formed on the walls of the lamp in those cases where carbon electrodes were used, but in all cases it was so rapid that after a few hours of operation the light from the lamp would be almost entirely cut off. The accumulation of the deposit was gradual and rather uniform. No particles of carbon could be observed, but the globe would first take a uniform brown shade, which would gradually increase until it was absolutely black.

Regarding the statement that there may have been some oxygen in the lamp during the demonstration this evening, I wish to bring out that it was undoubtedly the case, owing to the leaks in the apparatus. The spectrum, however, as far as the eye could determine, was substantially the same as that given out regularly

by the titanium bromo-chloride. As brought out in the paper, however, the spectrum does not appear to be that of tungsten, but with the exception of a few absorption lines is substantially a continuous spectrum. The flame surrounding the arc, however, usually shows some of the lines of the constituent elements.

(*Discussion at Washington, D. C., April 28, 1916.*)

O. H. ESCHHOLZ (*Communicated*): While rapid advances have been made in the incandescent lamp development, it is evident that its ultimate efficiency is determined by the filament

FIG. 12.

evaporation. Indications are, therefore, that investigations of the luminous radiations of incandescent vapors should result in a marked improvement in efficiency.

The growth of cathode and anode during lamp operation is worthy of comment. Fig. 12 shows a tungsten anode which has been modified to a considerable extent. The characteristic cubical structure of tungsten crystals on the electrode shank and the needle-like formation of the electrode end are very apparent. The small tungsten globules are crystals that have been melted by contact with the arc.

J. W. RICHARDS: In regard to the statement of the curious phenomenon of a glowing sphere between the arcs, that might suggest an analogy with the curious phenomenon found in nature as globular lightning. I do not know whether there is such an analogy, but it looks like one.

A. J. LIEBMANN (*Communicated*): Mr. Darrah has brought out, in a very clear, concise and interesting paper, several new points which seem to indicate that tungsten arcs in atmospheres of different kinds show very great promise. His researches have resulted in a lamp which can almost be pronounced a commercial success, and probably could be accepted as such if the expense for its production was not so high.

There is, however, a limit to the candle power and efficiency of the gas-filled lamps, and at this border line the territory for the new lamp of the kind constructed by Mr. Darrah begins. There cannot be any doubt that continued research along the lines indicated by him will lead to a lamp more efficient than the gas-filled incandescent lamp, especially a lamp of higher candle power values. The tungsten arc, in an atmosphere of certain light intensifying vapors, doubtless has a great future.

W. A. DARRAH (*Communicated*): Mr. MacKay's experience regarding the effect of halogen gases on hot tungsten agrees with my own as far as free chlorine, bromine, and iodine are concerned. The effect was practically absent, however, with most of the compounds used in the experiments outlined, probably because the affinity of the halogen for the element with which it was combined in the vapor was greater than for the tungsten. Whenever a free halogen was added, however, a rapid decomposition of the tungsten adjacent to, but not at, the hottest point, was noted. As I have pointed out, this was frequently accompanied by a needle-like crystalline growth, usually around the upper electrode. A theory which seems to be fairly well supported by observed facts is that the gaseous tungsten compounds formed by combination with the electrode are decomposed by the arc temperature and condense immediately on the relatively cool (though incandescent) electrode.

My experience leads me to think that this effect, as well as the chemical reactions involving the electrodes (aside from evapo-

ration), is largely independent of the current conduction, but almost entirely dependent upon the thermal reactions controlled by the dissociation temperatures of the compounds involved.

Referring to Mr. Mott's experiments, I believe that with some types of arcs the compound or form in which a material is introduced into an arc is of great importance. This is especially true of flame arcs and the iron oxide arc. In the case of the vapor arc I have not noted any close relation between the compound in which an element occurs and the amount of light produced.

It would seem that the results in the case of the flame arc could be very simply explained by taking into account the conductivity of the materials at high temperatures, volatility, dissociation temperature, and secondary reactions. Those elements which are fully oxidized, in the case of an arc in air, would naturally allow the fewest secondary reactions and other things being equal would, of course, give out least light in the arc. Peroxidized compounds, on the other hand, by breaking down allow dissociation and therefore tend to increase the illumination. Compounds of elements having a multiplicity of valences naturally tend to dissociate and recombine, thus giving out light at each of these secondary reactions.

Mr. Moore, in his very interesting discussion of the properties of carbon, has raised many vital questions relating to high temperature reactions. In reply to his questions, I would say that my experiments covered amorphous carbon, graphite, and *"graphitized carbon;"* from four representative manufacturers. Contrary to expectations, graphite was not nearly as satisfactory as amorphous carbon, because it was mechanically weak, especially when in the presence of the liquid chlorides used. The amount of deposit on the globe was substantially the same with all forms of carbon. The deposit was not solely carbon, but appeared to contain carbides, reduced metals, and partial reduction products. In other words, the well-known property of heated carbon reducing many compounds practically excludes carbon from use in this lamp.

As pressures become lower, and fewer variables enter into an experiment, fundamental theories may be more readily applied. It is perhaps this fact which has facilitated the application of

the electron theory to the conditions in my lamp, for I have been able to explain many of the phenomena by the aid of this theory. As a matter of fact, however, the same phenomena can be explained equally well in ordinary chemical terminology without the assistance of the electron theory.

I do not think that the temperature of the tungsten vapor arc is determined by the volatilization temperature of tungsten, and in spite of the excellent heat conductivity of this metal, it is possible to have an intensely hot arc originating from a point in the electrode surface without raising the whole electrode to the boiling point.

One of the most serious early problems connected with this research was the heavy opaque deposit which formed on the walls of the globe. This factor, together with the changes and evaporation of the electrodes and consumption of the light intensifying vapors (the latter two being relatively small factors) controlled the useful life of the lamp. Recent researches I have conducted have opened up a method of eliminating the deposit on the walls of the globe, thus leaving as the vital points yet to be solved those relating to electrode changes and light intensifying vapors.

A paper read before the New York Section of the American Electrochemical Society, in Joint Session with the Illuminating Engineering Society, on November 11, 1915. Called up for Discussion at the Twenty-ninth General Meeting of the Society, in Washington, D. C., April 27-29, 1916.

NEW FORM OF COLOR-MATCHING LAMP.

By McFarlan Moore.*

Elaborate spectrophotometric investigations have been made to proving that all articles when viewed solely by the light of the tube lamp have exactly the same shades of color as they possess when viewed by the light of a clear sky. It is stated that all dyers and other color experts agree that the standard light which they wish for color judging is that entering a window from a clear north sky at an angle of about 45 degrees and preferably about mid-afternoon with a clear sun shining in the southwest.

The spectrophotometric curve of carbon-dioxide gas consists of a broken line with many jagged peaks, but an average of these peaks results in a smooth curve which gives a correct idea of the effective color characteristics so that it should be used to compare with the spectra of other sources. The effect of the banded character of the CO_2 spectrum, the tabulation of which consists of a broken line, was thoroughly investigated to determine its relation to the color-matching properties of the lamp.

The following samples of colored silk, taken from the National Color Card of America, were selected to represent all parts of the spectrum, and were spectrophotometrically tested to determine what the actual color composition was: Violet, National blue, Yale blue, emerald, lemon, orange and scarlet.

The results of each of these tests were carefully plotted in the form of a curve, and a review of the data obtained in connection with these reflection curves shows that the irregularities in the CO_2 spectrum are absolutely without visible effect, and that they deviate only very slightly from north-sky values to which they are compared. It has been pointed out that if these north-sky values had all been taken at an angle of about 45 degrees, there would

* The following is a condensation of Mr. Moore's paper. The full text can be found in the Trans. Illuminating Eng. Soc. for 1916.

have been no detectable variation, and that therefore the color-matching values of the CO_2 spectrum were all that could be desired.

Fig. 1 shows an exterior view of this new color-matching unit. The straight tube lamp is contained in an elongated sheet-metal

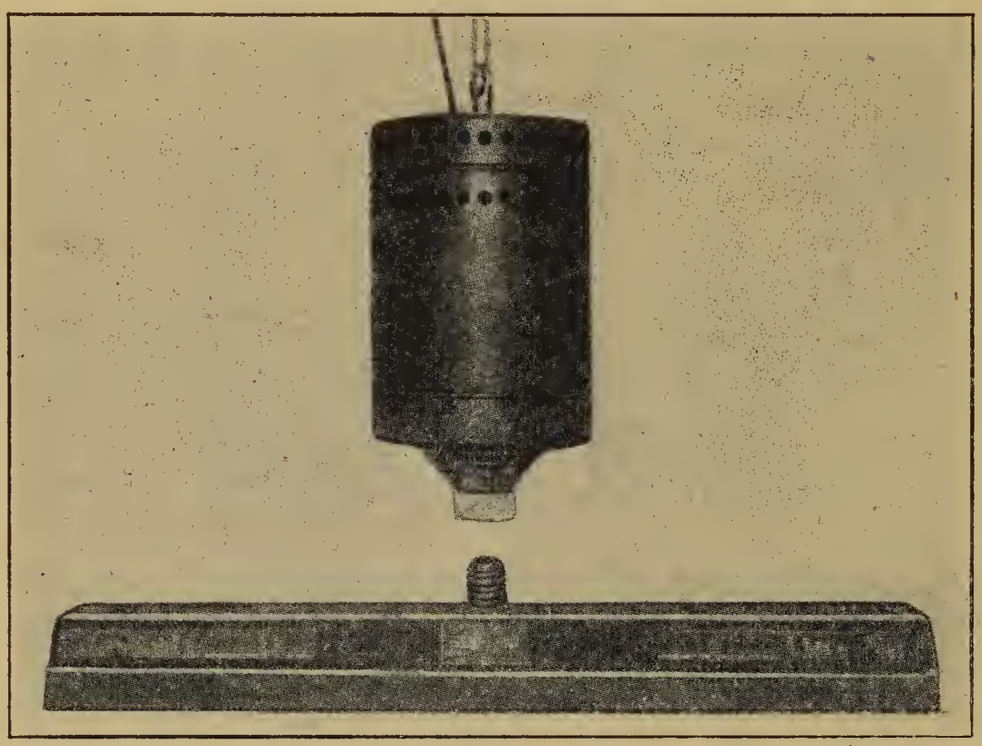

Fig. 1. Lamp with Transformer.

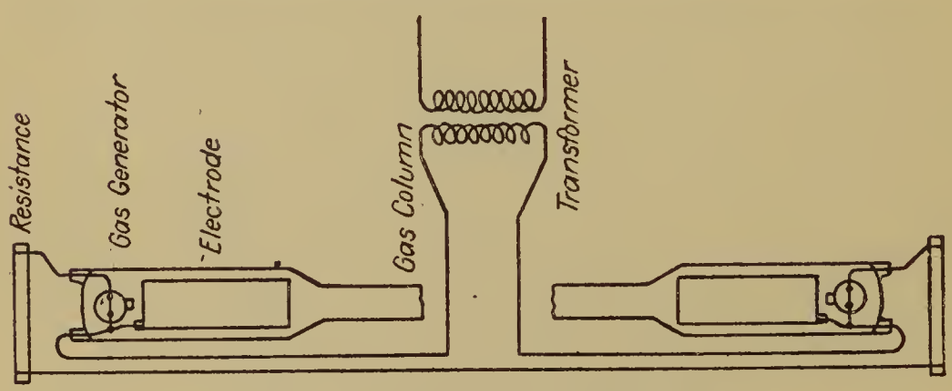

Fig. 2. Diagram of Connections.

case, which is provided with a screw base similar to that used on the larger sizes of incandescent lamps. Instead of the lamp being fed CO_2 gas by means of an electromagnetic feed valve, it is generated automatically within the tube itself. Near each electrode is placed a small bulb about an inch long, containing calcium carbonate, from which emanates CO_2 gas when the resistance wires imbedded in it became heated to exactly the proper degree by

reason of their being connected in shunt to the gas column. See Fig. 2. The gas column is 0.875 inch in diameter and one foot long, and appears as a solid bar of light of intense whiteness. The foot-candles available near the tube are over 200, thereby making this apparatus suitable for the very closest color discriminations. The degree of vacuum is automatically held within 0.001 of a millimeter, and the apparatus will stand wide line-voltage fluctuations without becoming disarranged in any way. The lamp takes about 240 watts.

Since light is the source of all color, it has been proposed that this new lamp receive official recognition from the International Conference on Electrical Units and Standards.

This new lamp is suitable for making absolutely correct color determinations, and is applicable to a very wide field, but is particularly useful in enabling the dye shops of the great textile industry to run night shifts.

Edison Lamp Works,
General Electric Company,
Harrison, N. J.

DISCUSSION.

(In New York City, November 11, 1915).

W. R. Mott: The Moore Carbon Dioxide White Light has an established useful field for color matching, secured by its excellent approach to daylight and to the light of the snow-white high-amperage flame arc.

Bloch (Elektrotechnische Zeitschrift (1913) p. 1306), and Jasse (same, page 145) gives the following data:

	Red	Green	Blue
Daylight, clouded sky	0.333	0.333	0.333
Daylight, blue sky	0.272	0.337	0.391
Moore light with carbon dioxide	0.290	0.342	0.368

The position of the Moore tube is between that of daylight with clouded sky and blue sky. The light of the snow-white flame arc is extremely close to daylight.

The snow-white flame arc is used in lithographic work, in front of jewelry stores, in fish markets, etc.

The spectrum of the snow-white flame arc is made up of thousands of emission lines set so close as to very closely duplicate the practical effects of the continuous spectrum. The approach to daylight is also very close in the ultra-violet. For these reasons, and its wonderful efficiency, the white-flame arc gives the best test of dye fading of any known artificial light. (See paper W. R. Mott—Trans. Am. Electrochem. Society (1915) **28**, 371). I expect that dye houses will find it very satisfactory to make a combined use of the flame arc for dye-fading tests and color matching. As to efficiency for producing daylight light, the white flame high-amperage lamp is three to ten times better than other light sources.

In the Illuminating Engineer (London) 1912, **5**, 465, the following data are given on the Moore carbon dioxide tube:

Phase	Length of Tube	Candles (Hefner)	K. W. Consumed
Single	66 ft.	800	2.8–3.2
"	83 "	1,000	3.1–5.5
"	100 "	1,200	3.6–3.75
Three	125 "	1,500	4.0–4.7
"	150 "	1,800	4.5–5.4

"On this basis, the specific power consumption would be about 3½ watts per English candle."

The results on the white-flame arc and blue-globe gas-filled tungsten lamp (See Lighting Journal, Oct. 1915, p. 228) are given below:

	Line Volts	Arc Volts	Mean Spherical Candlepower	Line Watts per M. S. C. P.
White-flame arc (open)	115	63	5,130	0.63
Gas-filled tungsten globe, blue	115	115	485	2.00

Of course, the efficiency of the incandescent lamp can be raised by increased line voltage, but at a material reduction in life. The flame arc can be very considerably increased in efficiency by several factors. The rapid development of the high-amperage white-flame arc is shown by the large number of firms now making high-amperage lamps to burn white-flame carbons.

In conclusion, all these lighting devices have certain particular fields of best merit. The Moore tube gives a soft diffused light.

The gas-filled tungsten lamp has elements of convenience that appeal strongly for use in dry-goods stores. The flame arc is notable for efficiency and quality of light and its portability for units of 5,000 and greater candle power.

W. C. Moore: If a man wants a light which is fairly close to the morning-sky light, he can get it with the white-flame arc; if he wants a light which is close to noon-sun light, he can get that also with the flame arc, so that the flaming arc is more flexible as far as the quality of light goes than any of our other illuminants. I noticed also in this tube that in being started up that there was considerable lag, and that it did not come up quickly to its full value. I would like to ask Dr. Moore how long it takes the tube generally to come up to the full value of the light, and in that connection I would point out that the flaming arc will come up to its full value almost immediately, in fact, so quickly that you cannot detect any time at which it is not at its full intensity.

I would also like to ask Dr. Moore what is the largest gap in the spectrum between any of the lines, and whether they come across any colors which happen to be so nearly monochromatic that they dodge in between any of these lines.

McF. Moore: In reference to Mr. Mott's discussion, practically nine-tenths of what he said seems to be an agreement with what I tried to say. In reference to the efficiency, there is no question but that the efficiency of the flame arc is very high, but there is a great question whether efficiency plays any part whatsoever. I have been in this color manufacturing game for some years, and I have never yet found a single instance commercially where the efficiency played any part whatsoever. What the man who is interested in color from a business standpoint wants is something that will enable him to keep his dyeshop open all night.

In reference to the lag that Mr. Moore speaks of, normally with this type of lamp, it will require about four minutes, however, it is very easy, by simply reducing the diameter of the resistance wire to start it in less than one-half a minute, but that requires a higher resistance; in other words, the starting is entirely a function of first cost and the dyer has little interest in that. He turns on his lamp in the morning and he lets it run as long as he

wishes it and after it has once started, then it will start promptly at any time after the case is thoroughly heated up.

In reference to Mr. Moore's question, I would like very much to have read the whole of Mr. F. A. Benford's report, since he very carefully selected samples from the standard color cards of America to represent each portion of the six spectrums, and it was impossible for him to find any color where there was any possibility of detecting any difference in the color values.

Dr. Nutting of the Bureau of Standards stated sometime ago that the fact that the two spectrums were different could not be detected as regards the color values, but that has required the splendid work of Mr. Benford.

F. A. Benford: In respect to the effect of the gaps in the spectrum, the data was not in such shape that I could analyze that very closely, but with the figures and data I have, the greatest deviations from new-sky light amounted to about three percent, due to the gaps in the spectrum, and under the circumstances I could not ascertain whether that three percent was one percent or five percent, and I could hardly be certain that you could really see the difference. I found that the reflection characteristics of the materials tested did not show any strong selective bands. None of the samples tested actually went down to zero at any point in the spectrum, and the slopes were very smooth, there were no humps or color spots at any place in the reflection characteristics. I do not believe that you could ever get a surface selective enough to match up with the high and low points in the spectrum, and thus give you a difference in the apparent color value from sky light.

W. C. Moore: What is the largest gap, expressed in microns, between any two lines?

F. A. Benford: I cannot give you that specifically because the line varies intensely, and I would not like to say; in fact I can not say where is the biggest gap; the lines fade out from very bright lines to very fine, and apparently there is no place where there is not a line within say two or three hundredths of a micron. That point I did not look into very closely, because I was interested only in getting an average intensity over certain specific

ranges of the spectrum, and as long as I divide the spectrum into twenty-two parts, as is shown in the test curve, and as long as none of those twenty-two parts fall off very much, we know that there is no large region in the spectrum which is weak or extra strong. The lines may be located on one side or the other of those regions tested, but I do not think that that will make the least bit of difference in the lamp as a color matcher; the average would not have been changed.

W. C. MOORE: With respect to the efficiency, we expect to see in the near future quite a development of the white-flaming-arc lamp for color testing, that is, for determining the fastness of color.

We have made a very large number of experiments at Cleveland along this line, and you can very well see that when you are using an illuminant which not only will give you an idea of the resistance of your color to light, but which may also be used for color matching, that you have a fine combination; and it is especially in the color-fading tests that the efficiency of the white-flame arc would stand out.

C. G. FINK: That is undoubtedly true in the case of the white-flame arc. It is a point in its favor.

(In Washington, D. C., April 28, 1916).

CHAIRMAN C. G. FINK: This is primarily an illuminating engineering paper, but there are several points in it which ought to interest the electrochemist.

There are two points, in particular, which are referred to, the electrodes and the mode of feeding the tube with gas. The electrodes have heretofore been carbon. Mr. Moore has left the carbon electrode and has gone over to other materials. The electrode described in the paper is an aluminum one, and that is the electrode which has given very successful results after trying perhaps ten or twenty others. The problem is to find an electrode which will not readily disintegrate in an atmosphere of carbon monoxide and carbon dioxide.

Another point of interest to the electrochemist is "feeding" the tube with CO_2 gas. The old method used to be an electro-magnetic valve, with which most of you are familiar; carbon dioxide was

generated by dropping hydrochloric acid on limestone. The new method of supplying fresh quantities of CO_2 described in the paper is rather ingenious, at least to my knowledge it has not been tried in a tube of that kind before. Mr. Moore shunts the tube and passes a current through a small coil of nichrome wire imbedded in finely divided calcium carbonate. As soon as the CO_2 in the tube grows less, the current through the nichrome wire increases, heats the calcium carbonate, and a fresh supply of CO_2 is introduced into the tube. This is a little apparatus which might be used to advantage in other cases. I wanted to emphasize these two particular points—the electrode and the method of "feeding" the tube with CO_2.

CORRECTIONS.

The discussion on pages 38 to 40 by W. H. Walker has inadvertently been printed from the stenographic report without previous revision by the author.

On page 48 at the beginning of the last paragraph insert F. A. LIDBURY: The discussion beginning with this paragraph has been offered by Mr. F. A. Lidbury instead of Dr. C. Hering as it now appears.

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